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SYNTHESIS OF THERMALLY STABLE POLYMERS

WRIGHT STATE UNIVERSITY
DAYTON, OHIO 45435

JULY 1978

TECHNICAL REPORT AFML-TR-78-98
Final Report for Period 1 January 1976 — 31 March 1978

AIR FORCE MATERIALS LABORATORY
AIR FORCE WRIGHT AERONAUTICAL LABORATORIES
AIR FORCE SYSTEMS COMMAND
WRIGHT-PATTERSON AIR FORCE BASE, OHIO 45433

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A number of novel reactions with ambient temperature cure potential were
investigated. The most promising system consisted of the formation of
alkynyl-substituted polyurethanes which underwent base-catalyzed, intramolecu-
lar-cycloaddition cures to afford the corresponding polyoxazolidones. With
the specific systems synthesized, however, intramolecular-cycloaddition cures
were achieved only in solution.

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FOREWORD

This report was prepared at Wright State University, Dayton, 45435, under AF Contract No. F33615-76-C-5084. The Contract was initiated under Project No. 7342, "Nonmetallic and Composite Materials", Task No. 734201, direction of the Air Force Materials Laboratory, Dr. F. L. Hedberg, (AFML/LNP), Project Engineer.

This report covers work conducted from 1 January 1976 to 31 March 1978. It was released by the authors April 1978.

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SECTION I
INTRODUCTION

The major objective of this research was the preparation of thermally-stable adhesive systems that cure at ambient temperature without the evolution of volatiles and exhibit high-strength properties at elevated temperatures. These resins are needed to facilitate field repair in structural components of U.S. Air Force flight vehicles. Current state-of-the-art adhesive resins that cure at ambient temperature require an extended time interval for the completion of the cure and have limited elevated temperature capability before suffering a drastic loss of strength properties.

Three different approaches to new adhesive systems were investigated. The first involved the cycloaddition of chemical reagents to liquid unsaturated polymers. Reactions were used that proceed at ambient temperature without the evolution of volatiles to afford cyclic and bicyclic structures. It was postulated that the rigidity of the polymer backbone and, hence, its glass transition temperature (Tg) would substantially increase as the cycloadditions proceeded.

In the second approach, the polymerization of diisocyanates with diepoxides was investigated. The polymerizations, which proceed without the evolution of volatiles, produce polyoxazolidones that are thermally stable and have good mechanical properties.[1-3] Although several catalysts are known to enhance the rate of polymerization, the reaction is still very slow at ambient temperature. It was postulated that, if the reaction could be further enhanced so that high-molecular-weight resins were produced rapdily at ambient temperature, the polymerization of two liquid monomers in place would afford a convenient means of applying a high-temperature adhesive. Hence, a search for more effective catalysts was carried out.

The third approach involved the synthesis of polymers that undergo low-temperature, chemically-induced, intramolecular cyclization reactions. The intramolecular cyclizations, which occur at pendent sites on the backbone without the evolution of volatile by-products, were designed to produce fused, linear polymer structures with Tg's above 350°F.

A second objective of this research was the preparation of novel, thermally-stable transparent materials that display a high degree of impact and abrasion resistance. The requirements of current and future supersonic aircraft for transparent plastic materials that can be used in thermooxidative

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environments above 350°F have created a pressing need for research in this area. Currently available materials, such as, the acrylics and poly-carbonates, are experiencing great difficulty in meeting the elevated temperature and environmental resistance requirements associated with advanced aircraft.

The major approach to the new transparent materials involved the optimization of the synthesis of the aromatic ionomers prepared under contract F33615-75-C-5073.[4] An investigation to determine the most effective route for crosslinking the transparent phenylated polyimides prepared under Contract F33615-75-C-5073 was also conducted. This work involved the thermal polymerization of ethynyl and phenylethynyl groups that were incorporated along the polyimide backbone.

SECTION II

DISCUSSION

A. Preparation of New Adhesive Systems

1. Cycloaddition of Chemical Reagents to Liquid Unsaturated Polymers

The first system that was evaluated involved the Diels-Alder cycloaddition of conjugated dienes to highly-unsaturated polyester resins. Polyester $\underline{3}$, which was prepared by the polymerization of maleic anhydride ($\underline{1}$) and ethylene glycol ($\underline{2}$), was selected as the initial candidate resin.[5] Model reactions of

$$\underline{1} \qquad\qquad \underline{2} \qquad\qquad\qquad \underline{3}$$
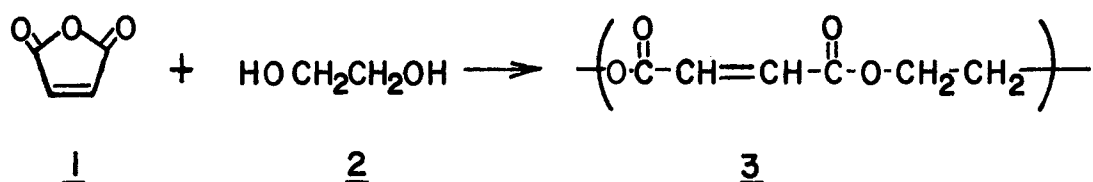
2,3-dimethyl-1,3-butadiene ($\underline{4}$) and furan ($\underline{7}$) with diethylmaleate <u>at room temperature</u>, however, failed to produce the cyclic adducts $\underline{6}$ and $\underline{8}$. Similarly,

$$\underline{4} \qquad\qquad\qquad \underline{5} \qquad\qquad\qquad\qquad \underline{6}$$

$$\underline{7} \qquad\qquad \underline{5} \qquad\qquad\qquad \underline{8}$$
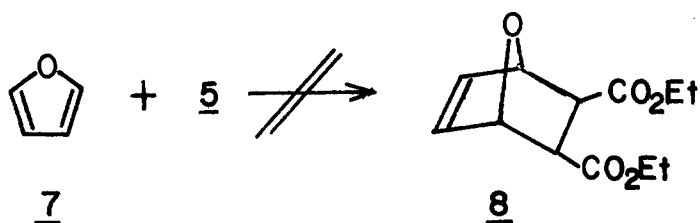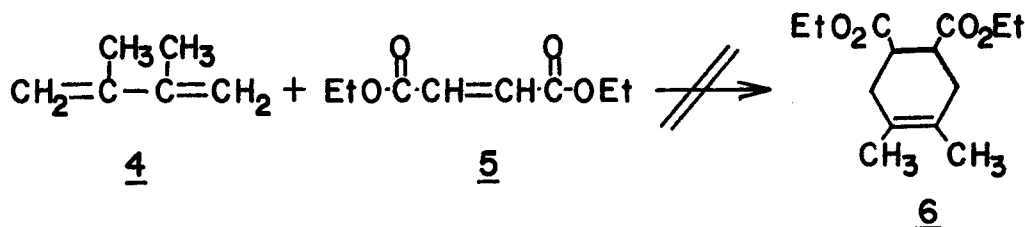
treatment of resin $\underline{3}$ with $\underline{4}$ and $\underline{7}$ at room temperature resulted in no detectable changes in the resin's properties.

The possible use of the 1,3-dipolar cycloaddition of nitrile oxides to ethynyl groups as a cure reaction was then investigated in the model reaction of benzonitrile oxide ($\underline{9}$) with 2-butyn-1,4-diol ($\underline{10}$). The exothermic reaction, which was carried out in acetone at room temperature, produced the yellow, oily adduct $\underline{11}$.

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$C_6H_5\text{-}C\equiv N\rightarrow O$ + $HOCH_2\text{-}C\equiv CCH_2OH$ $\longrightarrow$

[structure **11**]

$\underline{\mathbf{9}}$ $\quad\quad\quad$ $\underline{\mathbf{10}}$ $\quad\quad\quad\quad\quad\quad\quad\quad\quad$ $\underline{\mathbf{11}}$
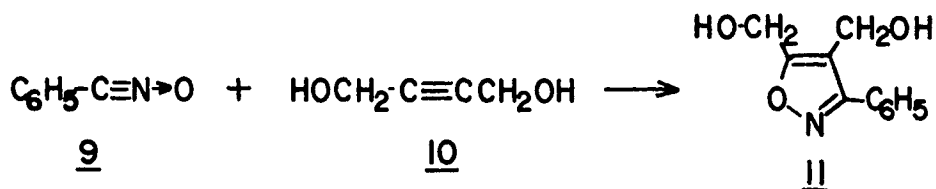
Phthalic anhydride ($\underline{12}$) was then polymerized with $\underline{10}$ to afford the liquid polyester $\underline{13}$.[6] The dark brown polymer is soluble in common organic solvents and has a number-average molecular weight of approximately 4800.

[structure **12**] + $\underline{10}$ $\longrightarrow$ [structure **13**: $-O\text{-}CH_2\text{-}C\equiv C\text{-}CH_2O-$]

$\underline{\mathbf{12}}$ $\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad$ $\underline{\mathbf{13}}$
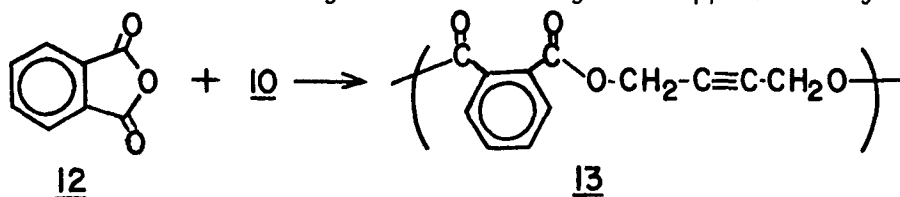
The differential scanning calorimetry (DSC) thermogram of $\underline{13}$ shows a strong baseline shift near -38°C (Figure 1). The alkynyl resin was treated with benzonitrile oxide at room temperature to give the polymeric adduct $\underline{14.}$ The soft, rubbery polymer is soluble in common organic solvents. The DSC thermogram of $\underline{14}$ shows a strong baseline shift near 14°C (Figure 1). Thus, the curing reaction afforded a 50 to 55°C increase in the resin's Tg.

$\underline{13}$ + $\underline{9}$ $\longrightarrow$ [structure **14**]

$\underline{\mathbf{14}}$
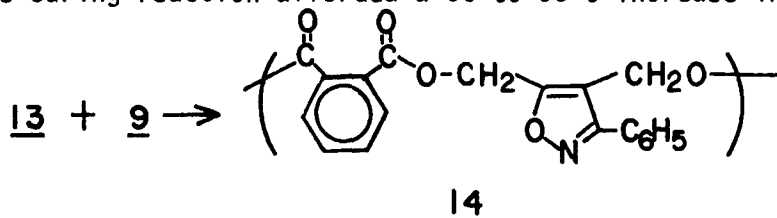
A second type of unsaturated resin ($\underline{16}$) was prepared by treating furfuryl alcohol ($\underline{15}$) with phosphoric acid.[7] The dark-red viscous polymer has softening point below 0°C (Figure 2) and is soluble in common organic solvents.

[structure **15**: CH_2OH] $\longrightarrow$ [structure **16**: CH_2]

$\underline{\mathbf{15}}$ $\quad\quad\quad\quad\quad\quad\quad\quad$ $\underline{\mathbf{16}}$
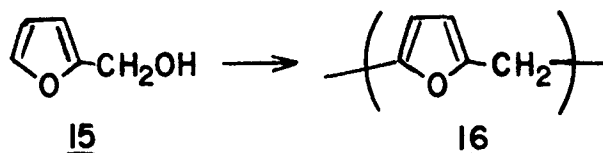
Since furan and alkyl-substituted furans readily undergo Diels-Alder reactions with electron-deficient dienophiles to form 1:1 and 2:1 cyclic adducts[14], it was postulated that the reactions of $\underline{16}$ with such dienophiles would proceed at room temperature and result in large increases in the polymer's Tg. For example, diethyl azodicarboxylate ($\underline{17}$) has been reported

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to react with furan at room temperature to produce a cyclic adduct.[8]
Treatment of polymer 16 with 17 resulted in an immediate exothermic
reaction that afforded a hard brown solid product. Although the product
was not completely characterized, it appears to have structure 18.

16 + EtO₂C—N=N—CO₂Et ⟶ [structure 18]

17   18
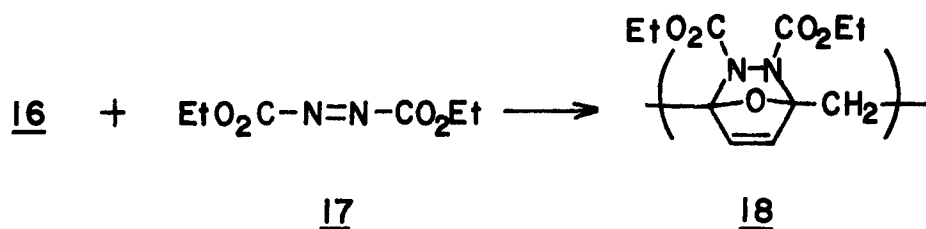
The polymeric adduct is soluble in common organic solvents and adheres
well to glass and metal. The NMR spectrum of 18 contains no absorptions
at 6.1δ where the furyl proton absorptions of polymer 16 appear. The DSC
thermogram of 18 shows a strong baseline shift between 20 and 30°C indicating
a low Tg (Figure 3). The thermogravimetric analysis (TGA) thermogram shows
a weight loss beginning slightly above room temperature.

The poly(alkylfuran) was also treated with 4-phenyl-1,2,4-triazoline-
3,5-dione (19). In this case, the azodienophile was insoluble in the resin
and no reaction occurred. However, when 19 was dissolved in a small amount
of acetone and added to 16 an immediate exothermic reaction took place to

16 + [structure 19] ⟶ [structure 20]

19   20
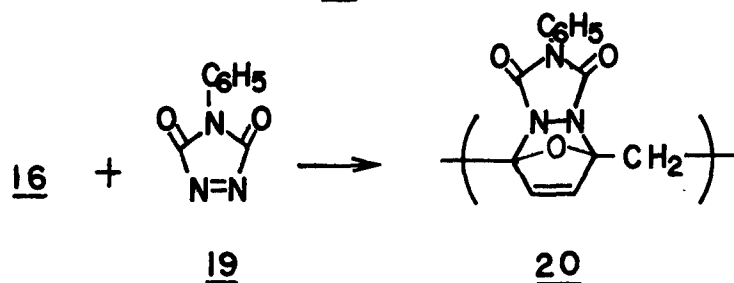
afford a hard brittle solid. The polymeric adduct, which is presumed to
have structure 20, is soluble in common organic solvents. The DSC
thermogram of 20 shows a strong base line shift near 70°C followed by a
strong exotherm with a maximum near 200°C (Figure 3). The TGA thermogram
obtained in air shows a gradual weight loss beginning near 80°C with the
polymer losing approximately 7% of its weight by 200°C (Figure 4).

Maleic anhydride (1) has also been reported to undergo a facile Diels-Alder reaction with dimethylfuran.[9] Hence, the anhydride was added to the liquid 16, and the resulting homogeneous mixture allowed to stand at room temperature overnight. No immediate reaction was observed, however, the mixture slowly solidified to yield the polymeric adduct 21. Polymer 21 is soluble in common organic solvents and adheres well to glass and metals.

16 +
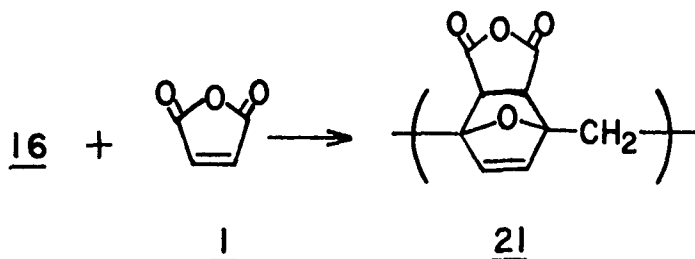
The infrared and NMR spectra of 21 are nearly identical to those reported for the dimethylfuran-maleic anhydride adduct. The DSC thermogram shows a strong baseline shift near 70°C followed by an exotherm with a maximum near 110°C (Figure 5). The TGA thermogram obtained in air shows that a weight loss accompanies this exotherm with the polymer losing 18% of its weight by 200°C (Figure 6). Polymer 16 and 1 were also allowed to react in ether at room temperature. The DSC and TGA thermograms of the product obtained were nearly identical to those of the adduct formed in the absence of solvent. Gel permeation chromatography (GPC) studies showed that the cured polymer had a molecular weight 500 to 700 higher than the uncured resin. The polymeric adduct formed in solution, however, was brittle and had poor adhesive properties compared to the polymer formed in the neat reaction. It is likely that the extent of reaction was less in the absence of solvent.

As part of the study to determine the most effective curing agents for polymer 16, the syntheses of two electron-deficient acetylenic were carried out. Treatment of ethyl phenylpropiolate (22) with concentrated ammonium hydroxide at room temperature provided an 84% yield of amide 23.[10] Subsequent dehydration of 23 with phosphorous pentoxide at 170-190°C gave a 77% yield of phenylpropionitrile (24).[11]

$$C_6H_5C\equiv C-CO_2Et \longrightarrow C_6H_5C\equiv C-CONH_2 \longrightarrow C_6H_5-C\equiv C-C\equiv N$$

22   23   24
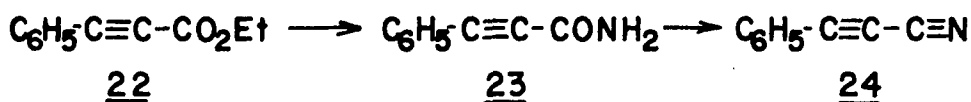
Similarly, treatment of dimethyl acetylenedicarboxylate (25) with concentrated ammonium hydroxide at -10°C gave a 90% yield of diamide 26.[12] Dehydration of 26 with phosphorous pentoxide according to known procedures, however, gave only trace amounts of impure product.[11-13] Dicyanoacetylene (27) was prepared in 32% yield by dehydrating the diamide with polyphosphate ester at elevated temperatures.[12,15]

$$CH_3O\text{-}\overset{O}{\overset{\|}{C}}\text{-}C\equiv C\text{-}\overset{O}{\overset{\|}{C}}\text{-}O\text{-}CH_3 \rightarrow H_2N\overset{O}{\overset{\|}{C}}\text{-}C\equiv C\text{-}\overset{O}{\overset{\|}{C}}\text{-}NH_2 \rightarrow N\equiv C\text{-}C\equiv C\text{-}C\equiv N$$

<center>25   26   27</center>
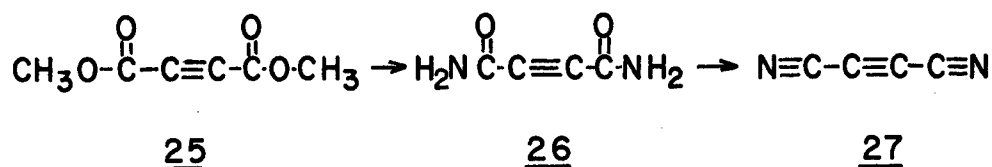
Polymer 16 was then treated with 24 and 27, and the resulting mixtures allowed to stand at room temperature for 2 days. Unfortunately, no changes in the physical state of the resin were observed in either case.

A third type of liquid unsaturated polymer was prepared by the free-radical polymerization of phenylacetylene (28).[16] The polymerization was carried out

$$C_6H_5\text{-}C\equiv C\text{-}H \longrightarrow \left(\text{-}CH=\overset{C_6H_5}{\overset{|}{C}}\text{-}\right)$$

<center>28   29</center>
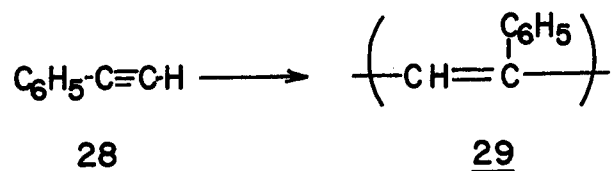
in toluene at 60°C to afford a low-molecular-weight viscous oil. Attempts to cure polymer 29 via Diels-Alder reactions with maleic anhydride, tetracyanoethylene, and phenyl acetylene were unsuccessful. Evidently the resonance stabilization of the conjugated double bonds prevents them from undergoing cycloadditions.

The last system investigated involved the synthesis and polymerization of aromatic acetylenic ethers. Phenoxyacetylene (30) has been reported to polymerize spontaneously on standing at room temperature to give a dark-red liquid that partially solidifies upon further standing to afford an insoluble black precipitate.[17-19] The thermal polymerization, which requires from 7 to 10 days at room temperature, has been studied extensively. It has been postulated that the red viscous oil produced initially is the linear polymer 31. Inter- or intramolecular cyclization is thought to occur when

$C_6H_5OC{\equiv}CH \rightarrow$ structures $\rightarrow$ structures $\rightarrow$ structures

30	**31**	**32**	**33**
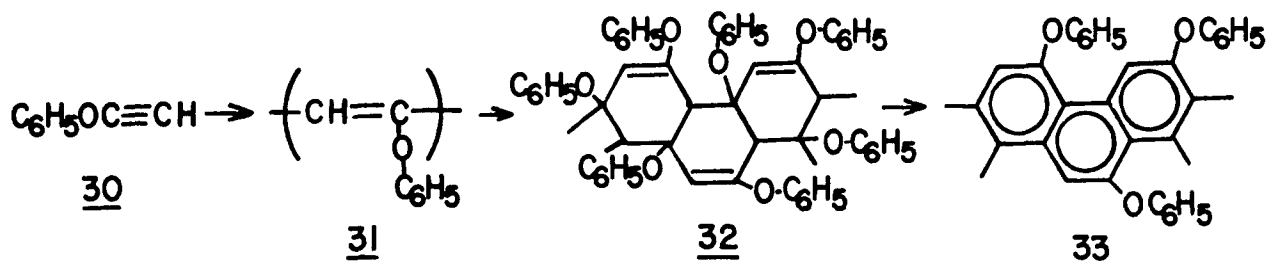
<u>31</u> is heated or allowed to stand at room temperature for long periods of time. The cyclic products produced undergo dephenolation when heated to high temperatures to form condensed aromatic structures such as <u>33</u>.[19]

Phenoxyacetylene was prepared by the following reaction sequence. The reaction of vinylacetate (<u>34</u>) with phenol (<u>35</u>) in the presence of mercuric acetate and sulfuric acid provided a 60% yield of phenyl vinyl ether (<u>36</u>).[21] Treatment of <u>36</u> with bromine at 0°C gave the dibromo compound <u>37</u>.[22] Dehydrohalogenation of <u>37</u> with 85% potassium hydroxide gave a very low yield of the alkyne. Compound <u>38</u>, however, was prepared in 52% yield by allowing <u>37</u> to react with sodium amide in liquid ammonia.[20]

$CH_3\text{-}C(O)\text{-}O\text{-}CH{=}CH_2 + C_6H_5OH \rightarrow C_6H_5O\text{-}CH{=}CH_2 \rightarrow C_6H_5O\text{-}CH(Br)\text{-}CH_2Br \rightarrow C_6H_5O\text{-}C{\equiv}CH$

34	**35**	**36**	**37**	**38**
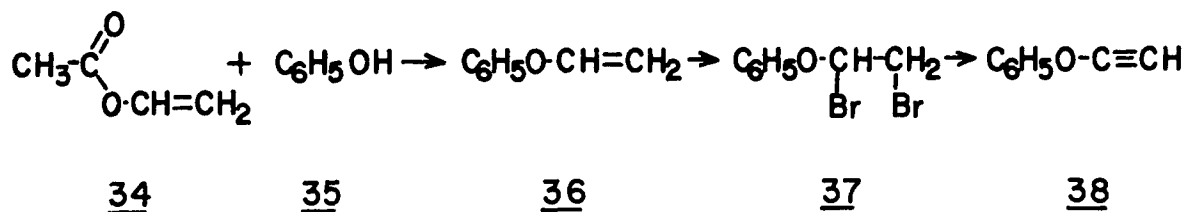
In order to facilitate the polymerization of <u>30</u> at room temperature, the use of inorganic catalysis was investigated. The polymerization had been carried out previously using a variety of catalysts.[17-19] The polymers obtained had similar structures to those produced thermally, but they had much lower molecular weights. On fact, all of the previously employed catalyst systems had afforded dimers or trimers, except a triethylaluminum-titanium chloride system that at -70°C gave polymers with molecular weights as high as 5000.[18]

Since Palladium (II) readily forms complexes with acetylene and substituted acetylenes that are labile and polymeric [23,24] and since bis(benzonitrile) palladium chloride (<u>39</u>) has been reported to catalyze the trimerization of diphenylactylene to hexaphenylbenzene at moderate temperatures,[25] phenoxyacetylene was treated with a catalytic amount of <u>39</u>. A dark-brown precipitate formed immediately. The infrared spectrum of the

$$\underline{30} \ + \ Pd\,Cl_2(C_6H_5CN)_2 \longrightarrow \left(CH=\underset{\underset{C_6H_5}{|}}{\overset{|}{C}}\right)$$

$$\underline{39}$$
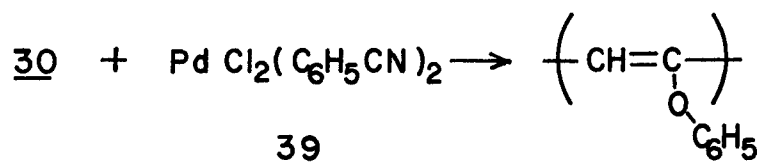
product is identical to that reported for poly(phenoxyacetylene). The polymer
is partially soluble in common organic solvents at room temperature and is
completely soluble in chlorinated hydrocarbon solvents at elevated
temperatures. The molecular weight of the fraction soluble at room
temperature was determined by GPC to be approximately 2000. The DSC
thermogram of the polymer shows a moderate exotherm with a maximum near
155°C (Figure 7). The TGA thermogram obtained in a nitrogen atmosphere
shows that a slight weight loss accompanies the exothermic process with the
polymer losing approximately 8% of its weight by 200°C (Figure 8). This
evolution of volatiles, which appeared to consist primarily of phenol,
precludes the use of the thermal cyclization as a cure reaction.

The unsaturated polymer was then treated with phenylacetylene (28).
However, no apparent reaction occurred at ambient temperature. A light brown
product (40) was obtained when 31 and 28 were stirred in refluxing
bromobenzene. The DSC spectrum of the polymeric adduct shows a baseline

$$\underline{31} \ + \ C_6H_5C\equiv CH \longrightarrow$$

40
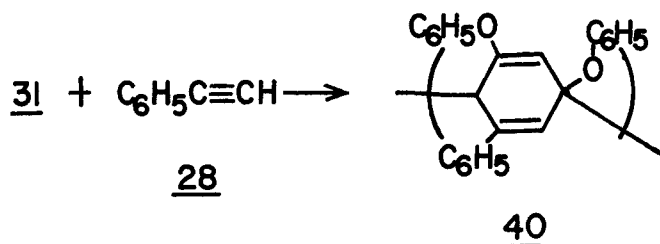
shift near 150°C, but it does not show the exotherm at 155°C, which is
characteristic of untreated poly(phenoxyacetylene) (Figure 7). The TGA
thermogram obtained in nitrogen shows a gradual weight loss beginning near
150°C (Figure 8). It is postulated that the adduct begins to aromatize
at this temperature via the loss of phenol.

$$\underline{40} \quad \xrightarrow{-C_6H_5OH} \quad$$
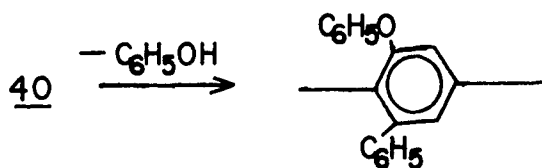
2. Polymerization of Diisocyanates with Diepoxides

As stated in the INTRODUCTION, diisocyanates undergo polymerization with diepoxides to afford polyoxazolidones.[1-3] The polymerizations are catalyzed by quaternary salts, such as, ethyl triphenylphosphonium bromide (ETPB). For example, toluene-2,4-diisocyanate (41) (TDI) has been polymerized with several commercially available diepoxides in the presence of ETPB to give the corresponding polyoxazolidones (42).[26] Although the known catalysts are
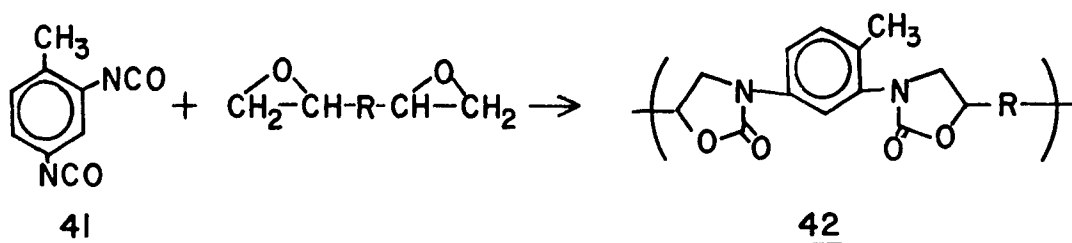
effective in producing polymers of moderate molecular weight, the polymerization is very slow at ambient temperature. Hence, a search for more effective catalysts was carried out.

The polymerization of 2,2-bis[4-(2,3-epoxypropoxy)phenyl] propane (43) (Dow Chemical DER 332) with TDI was carried out at ambient temperature in the presence of several phosphonium and sulfonium salts (Table 1). Tetrabutyl-phosphonium bromide was the most effective catalyst producing a viscous mixture in 2 hr and the solid polyoxazolidone 44 in 3 days. The DSC
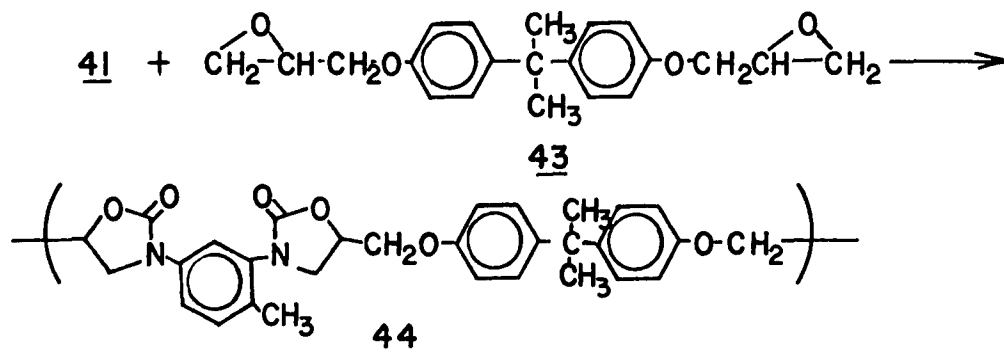
thermogram of the polymer, however, shows a baseline shift near 0° C (Figure 9). The TGA thermograms obtained in nitrogen and in air show an initial weight

10

TABLE I

EFFECT OF CATALYSTS ON THE POLYMERIZATION
OF DIEPOSIDES AND DIISOCYANATES

Catalyst[1]	Result
$C_2H_5\overset{+}{P}(C_6H_5)_3$ Br^-	Viscous after 1 day, solid after 1 week
$(C_4H_9)_4\overset{+}{P}$ Br^-	Viscous after 2 hr, solid after 3-4 days
$CH_3\overset{+}{P}(CH_6H_5)_3$ Br^-	Extremely viscous after 2 weeks
$(CH_3)_3\overset{+}{S}$ I^-	Viscous after 1 day, extremely viscous after 1 week
$(CH_3)_3\overset{+}{S}OI^-$	White brittle ppt after 1 week

(1) Concentration of 1% (w/w).

loss near 220°C with the polymer losing approximately 6% of its weight by 350°C (Figure 10). In order to determine if the low temperature transition observed with DSC was due to further polymerization, the monomers were allowed to react at 70°C and 150°C in the presence of tetrabutylphosphonium bromide. The polyoxazolidones obtained at these temperatures, however, still display a transition between 25 and 40°C.

3. Chemically-Induced, Intramolecular Cyclizations of Polymers

The use of a chemically-induced intramolecular cyclization reaction as a curing reaction for polyurethanes was investigated. Isocyanates add to 1-alkyn-3-ols to afford alkynylcarbamates, which upon treatment with base cyclize to the corresponding 4-methylene-2-oxazolidones.[27,28] The oxazolidone can be obtained in one step if the isocyanate and the alkynol are allowed to react in the presence of base. For this study, diisocyanates were to be polymerized with bisalkynols to afford alkynyl-substituted polyurethanes. It was postulated that these polymers would then undergo base-catalyzed intramolecular cyclizations to yield the corresponding polyoxazolidones.

a. Monomers

Three commercially available diisocyanates, i.e., toluene-2,4-diisocyanate (TDI), methylenedi-p-phenylenediisocyanate (MDI), and hexamethylenediisocyanate (HDI), were purchased for use in the study. The bisalkynol monomer 3,6-dihydroxy-3,6-dimethyl-1,7-octadiyne (47) was prepared by the reaction of acetonylacetone (45) with sodium acetylide (46) in liquid ammonia.[29]

$$CH_3\overset{O}{\overset{\|}{C}}-CH_2CH_2\overset{O}{\overset{\|}{C}}-CH_3 \;+\; Na^{\oplus}{}^{\ominus}C\equiv CH \longrightarrow CH_3\overset{OH}{\underset{C\equiv CH}{\overset{|}{C}}}-CH_2CH_2\overset{OH}{\underset{C\equiv CH}{\overset{|}{C}}}-CH_3$$

<div align="center">

45   46   47

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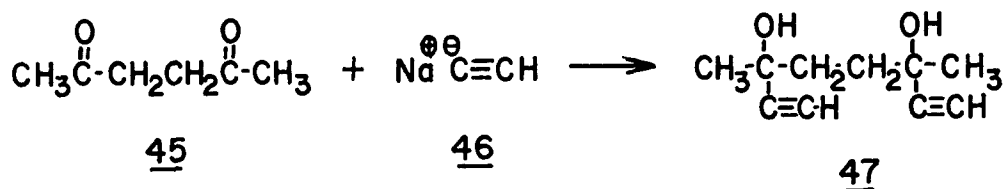
b. Carbamate and Oxazolidone Model Compounds

In order to determine the optimum experimental conditions for the polymerization of diisocyanates and bisalkynols, a series of model reactions was carried out. The model compounds obtained were thoroughly characterized so that their structures could be correlated with those of analagous polymers.

The addition of TDI (41) to 3-methyl-1-pentyn-3-ol (48) was attempted under a variety of reaction conditions (Table 2). None of the conditions used, however, produced good yields of 49.

$$41 \quad + \quad 2\ HO\text{-}\underset{\underset{C\equiv CH}{|}}{\overset{\overset{CH_3}{|}}{C}}\text{-}CH_2CH_3 \longrightarrow CH_3CH_2\underset{\underset{C\equiv CH}{|}}{\overset{\overset{CH_3}{|}}{C}}\text{-}O\text{-}\overset{\overset{O}{||}}{C}\text{-}NH \underset{CH_3}{\bigcirc} NH\text{-}\overset{\overset{O}{||}}{C}\text{-}O\text{-}\underset{\underset{C\equiv CH}{|}}{\overset{\overset{CH_3}{|}}{C}}\text{-}CH_2CH_3$$

$$\underset{48}{} \qquad\qquad\qquad\qquad\qquad\qquad \underset{49}{}$$
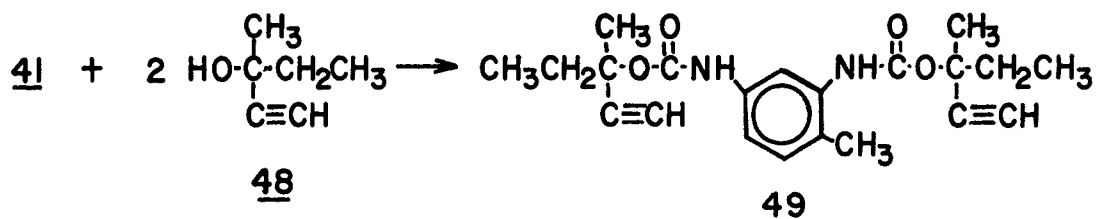
A 50-60% yield of a solid that displayed infrared absorptions characteristic of structure 49 was obtained when the reaction was carried out at ambient temperature in toluene containing triethylamine. Treatment of 41 with 48 in refluxing toluene containing triethylamine did provide a 78% yield of oxazolidone 50.

$$41 \quad + \quad 48 \longrightarrow$$

$$\underset{50}{}$$
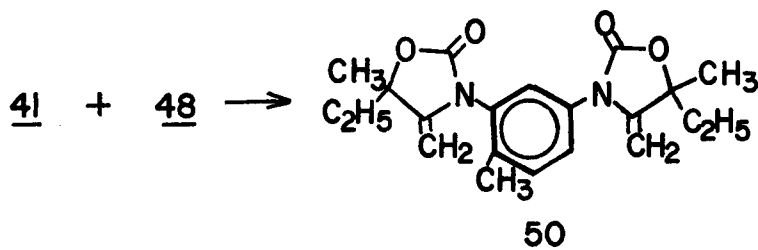
The addition of phenyl isocyanate (51) to 3,6-dihydroxy-3,6-dimethyl-1,7-octadiyne (47) was also carried out under several different reaction conditions (Table 2). A quantitative yield of carbamate 52 was obtained at 40°C in

$$2\ C_6H_5NCO \quad + \quad 47 \longrightarrow C_6H_5NH\text{-}\overset{\overset{O}{||}}{C}\text{-}O\text{-}\underset{\underset{C\equiv CH}{|}}{\overset{\overset{CH_3}{|}}{C}}\text{-}CH_2CH_2\underset{\underset{C\equiv CH}{|}}{\overset{\overset{CH_3}{|}}{C}}\text{-}O\text{-}\overset{\overset{O}{||}}{C}\text{-}NH\text{-}C_6H_5$$

$$\underset{52}{}$$
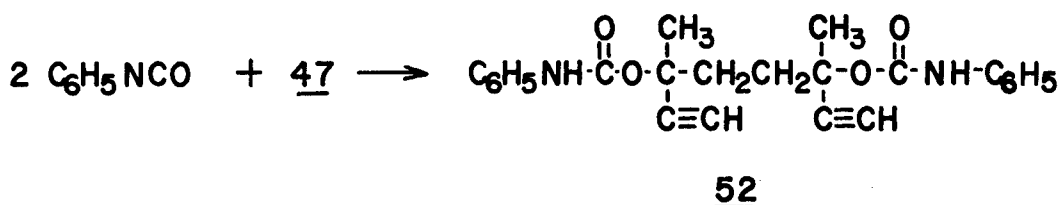
anhydrous dimethylformamide (DMF) containing tin octoate (Nuocure[R] 28). The reaction in anhydrous DMF at ambient temperature in the presence of diaza[2,2,2]-bicyclooctane (DABC) gave a crystalline product whose structure has not yet been determined. The infrared spectrum of this compound contains an absorption band at 1640 cm^{-1} that may be due to a urea carbonyl. The molecular

TABLE 2
MODEL COMPOUND STUDIES

Isocyanate	Alkynol	Solvent	Catalyst	Time/Temp. (hr/°C)	Product	Yield (%)
TDI	48	DMF	None	36/A[a]	Gel	
		NMP	None	6/A	NR[b]	
		Toluene	Et$_3$N	24/A	C[c]	50-60
		Cyclohexane	NaOMe	12/A	C + O[d]	
		NMP	NaOMe	24/A or 14/100	C + O	
		Toluene	Et$_3$N	24/110	O	78
PI[e]	47	Toluene	Et$_3$N	24/A	C + O	50-60
		NMP	None	6/A or 14/100	NR	
		DMF	Et$_3$N	24/A	C + O	
		DMF	DABCO	24/A	UK[f]	
		DMF	N28[g]	20/40	C	> 90
		DMF	None	24/70	C + O	
		NMP	NaOMe	12/A	UK	
		DMF	Et$_3$N	12/153	O	> 90
MDI	48	NMP	None	120/A	NR	
		Ether	None	24/A	NR	
		NMP	Et$_3$N	24/A	Gel[h]	
		NMP	DABCO	24/A	UK	
		DMF	N28	20/40	C	> 90
		Toluene	Et$_3$N	24/80	O	
		DMF	Et$_3$N	15/153	O	> 84
HDI	48	DMF	None	24/A	NR	
		DMF	N28	24/40	C	100
PrI[h]	47	DMF	Et$_3$N	32/153	O	> 90

a. Ambient temperature; b. No reaction; c. Carbamate; d. Oxazolidone;
e. Phenyl isocyanate; f. Structure not determined; g. Nuocure[R] 28 (tin octoate);
h. Formed upon addition of reaction mixture to water.

weight was determined by vapor pressure osmometry to be 558. Treatment of
47 with 51 in N-methylpyrrolidinone (NMP) at ambient temperature in the
presence of sodium methoxide gave a product that displays infrared absorptions
characteristic of both ethynyl and oxazolidone groups. The exact structure
of this compound has also not yet been determined. Oxazolidone 53 was
obtained in 90% yield by the reaction of 47 and 51 in refluxing DMF containing
triethylamine.

$$\underline{47} + \underline{51} \xrightarrow[\text{DMF},\Delta]{\text{Et}_3\text{N}} \text{C}_6\text{H}_5\text{-N} \cdots \text{-CH}_2\text{CH}_2 \cdots \text{N-C}_6\text{H}_5$$

<u>53</u>
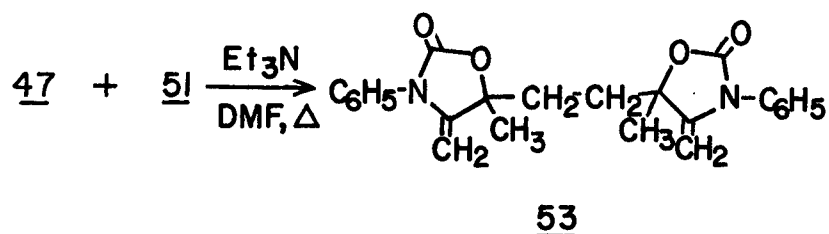
An investigation of the reaction of MDI (54) with 48 was then carried out
(Table 2). The best yields of carbamate 55 were obtained at 40°C in
anhydrous DMF containing Nuocure[R] 28. The addition of 54 to 48 in NMP

$$\text{OCN}\text{-}\bigcirc\text{-CH}_2\text{-}\bigcirc\text{-NCO} + \underline{48} \longrightarrow \text{C}_2\text{H}_5\overset{\text{CH}_3}{\underset{\text{C}\equiv\text{CH}}{\text{C}}}\text{-O-}\overset{\text{O}}{\text{C}}\text{-NH}\bigcirc\text{-CH}_2\bigcirc\text{-NH-}\overset{\text{O}}{\text{C}}\text{-O-}\overset{\text{CH}_3}{\underset{\text{C}\equiv\text{CH}}{\text{C}}}\text{-C}_2\text{H}_5$$

<u>54</u>   <u>55</u>
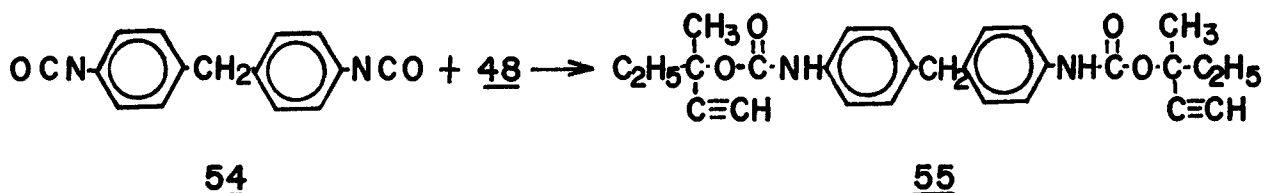
containing DABCO afforded another compound whose structure has not yet been
determined. The infrared spectrum of this compound is nearly identical to
that of 55. Treatment of 54 with 48 in refluxing DMF containing triethylamine
gave a good yield of oxazolidone 56.

$$\underline{54} + \underline{48} \xrightarrow[\text{DMF},\Delta]{\text{Et}_3\text{N}} \text{C}_2\text{H}_5\overset{\text{CH}_3}{\underset{}{\text{C}}} \cdots \text{N}\bigcirc\text{-CH}_2\bigcirc\text{N} \cdots \overset{\text{CH}_3}{\underset{}{\text{C}}}\text{C}_2\text{H}_5$$

<u>56</u>
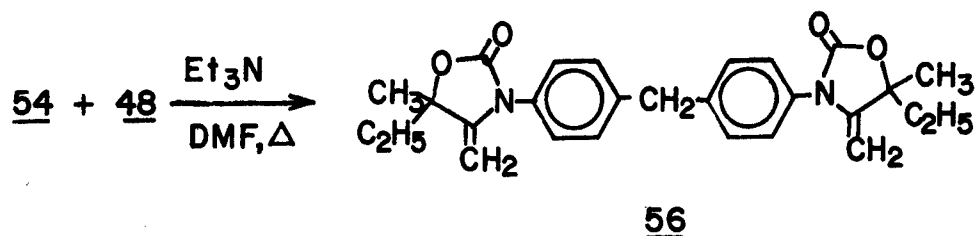
The preparation of all aliphatic model compounds was also investigated
(Table 2). The reaction of HDI (57) with 48 at 40°C in anhydrous DMF

15

containing Nuocure[R] 28 gave carbamate 58. Treatment of 47 with propyl isocyanate (59) in refluxing DMF containing triethylamine provided oxazolidone 60.

OCN CH$_2$(CH$_2$)$_4$CH$_2$NCO + 48 →

$$C_2H_5\text{-}\underset{C\equiv CH}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}\text{-}O\text{-}\overset{O}{\overset{\|}{C}}\text{-}NH\text{-}(CH_2)_6NH\text{-}\overset{O}{\overset{\|}{C}}\text{-}O\text{-}\underset{C\equiv CH}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}\text{-}C_2H_5$$

57

58

CH$_3$CH$_2$CH$_2$NCO + 47 →

60

59
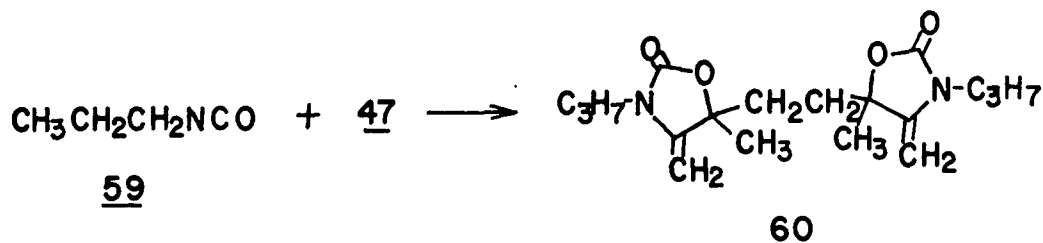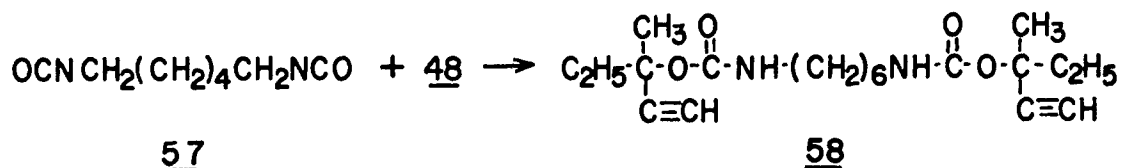
c. Polymerization of Diisocyanates with Bisalkynols

A study of the polymerization of diisocyanates with 3,6-dihydroxy-3,6-dimethyl-1,7-octadiyne (47) was conducted. The polymerization conditions were varied so that both alkynyl-substituted polyurethanes and polyoxazolidones were prepared.

The polymerization of TDI (41) with 47 was the first system studied (Table 3). Although the reaction was run with several different sets of experimental conditions, the polymerization afforded either low-molecular-weight

41 + 47 →

61
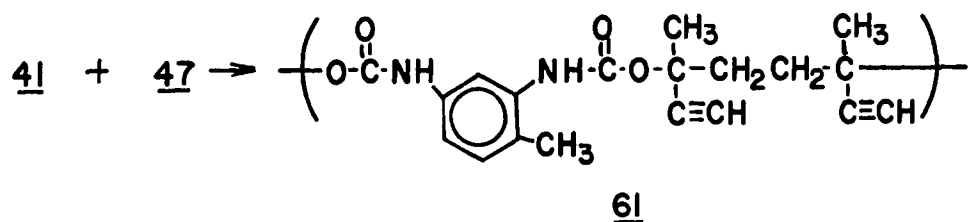
polymers or insoluble gels. The low molecular weights may be partially due to a steric hindrance between the methyl group in TDI and the tertiary alcohol. The insoluble gels obtained in DMF probably resulted from side-reactions of TDI with the solvent.

A thorough investigation of the polymerization of MDI (54) with 47 was then carried out (Table 3). The polymerization in DMF or NMP containing DABCO normally afforded insoluble gels. In one case, however, a polymerization at ambient temperature in NMP containing DABCO gave a gel that slowly dissolved

16

Table 3

POLYMERIZATION OF DIISOCYANNATES WITH 3,6-DIHYDROXY-3,6-DIMETHYL-1,7-OCTADIYNE

Diisocyanate	Solvent	Catalyst	Time/Temp. (hr/°C)	Product	η inh [a]
TDI	DMF	None	48/A [b]	Gel	
	NMP	None	24/A	U [c]	0.14
	NMP	None	72/A:24/50: 12/100	U + O [d]	0.10
	DMF	Et$_3$N	24/153	U + O	0.04
	Toluene	Et$_3$N	4/110	O	0.03 [f]
MDI	NMP	DABCO	96/A	U [g]	0.36
	DMF	DABCO	26/A	Gel	
	DMF	N28 [h]	120/A	U	0.38
	DMF	N28	144/A:24/30: 96/40	U	0.23
	DMF	N28	96/40	U	0.54
	MEK	N28	48/40	U	0.31 [f]
	S [i]	N28	60/40	U	0.27 [f]
	DMF	Et$_3$N	16/153	O	0.37
HDI	DMF	N28	65/40	U	0.25
	S + DMF [j]	N28	72/40	U	0.40
	DMF	Et$_3$N	24/153	O	0.07

a. Inherent viscosity; b. Ambient temperature; c. Polyurethane;

d. Polyoxazolidone; e. No reaction; f. Polymer precipitated from solution;

g. Polymer is probably branched; h. Nuocure[R] 28 (tin octoate); I. Sulfolane;

j. DMF was added 24 hr after the start of the polymerization

when stirred in excess solvent. The off-white product, which formed transparent, water-white films from acetone, had an inherent viscosity of 0.36 (0.250 g/dl in DMF at 30°C). Although the infrared spectrum corresponds closely to that

$$\underline{54} \;+\; \underline{47} \longrightarrow \left(\!O\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-N}H\!-\!\bigcirc\!\!-\!CH_2\!-\!\bigcirc\!\!-\!NH\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}O\text{-}\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle C\equiv CH}{|}}{C}}\text{-}CH_2CH_2\text{-}\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle C\equiv CH}{|}}{C}}\!-\!\right)$$

<p align="center"><u>62</u></p>
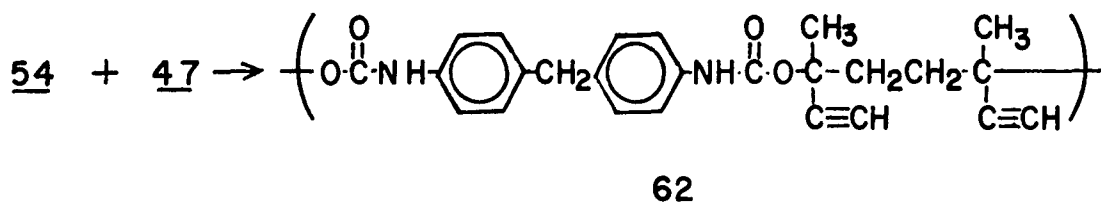
expected for structure <u>62</u>, the results of the model compound studies run in NMP containing DABCO and the fact that other polymers obtained under similar conditions were crosslinked suggest that the polymer is probably highly branched. A linear polyurethane was obtained from the polymerization of <u>54</u> and <u>47</u> in anhydrous DMF containing Nuocure[R] 28. The reaction was carried out at 40°C for 4 days to afford a nearly quantitative yield of <u>62</u>. The white, fibrous polymer has an inherent viscosity of 0.54 (0.6 g/dl in DMF at 30°C) and readily forms water-white transparent films from methyl ethyl ketone (MEK) solutions. The TGA thermogram obtained in an argon atmosphere shows a major weight loss beginning near 250°C (Figure 11). The DSC thermogram shows baseline shifts near 75°C and 135°C and a strong exotherm beginning near 175°C with a maximum near 226°C (Figure 12). The polymer's number-average molecular weight, which was determined by vapor pressure osmometry using MEK as the solvent, is approximately 5000. This is much lower than was expected due to the polymer's relatively high inherent viscosity and its ability to form excellent films. Evidently, the polymer backbone is quite rigid and, thus, very extended in solution.

The polymerization of <u>54</u> with <u>47</u> in refluxing DMF containing triethylamine afforded polyoxazolidone <u>63</u> in good yield. The polymer is soluble in

$$\underline{54} \;+\; \underline{47} \longrightarrow$$

<p align="center"><u>63</u></p>
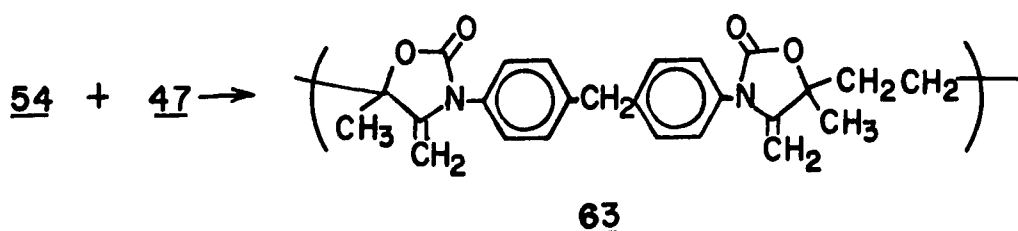
chlorinated hydrocarbon and amide solvents and has an inherent viscosity of

<p align="center">18</p>

0.37 (0.250 g/dl in DMF at 30°C). Transparent, water-white films can be cast from methylene chloride solutions. The DSC thermogram shows a strong baseline shift near 171°C (Figure 13). The thermal mechanical analysis (TMA) spectrum obtained with a penetration mode shows softening beginning near 167°C with the highest rate of penetration occurring at 177°C (Figure 14). The TGA thermograms obtained in air and argon show weight losses beginning near 225°C and 250°C, respectively (Figure 15).

In order to obtain alkynyl-substituted polyurethanes with low Tg's, the polymerization of HDI (57) with 47 was investigated (Table 3). A polymerization in anhydrous DMF containing Nuocure^R 28 that was run for 65 hr at 35-40°C provided a quantitative yield of 64. The white polymer has an inherent viscosity

$$\underline{57} + \underline{47} \longrightarrow \left(\begin{matrix} O & & O & CH_3 & & CH_3 \\ \| & & \| & | & & | \\ O\text{-}C\text{-}NH\text{-}(CH_2)_6\text{-}NH\text{-}C\text{-}O\text{-}C\text{-}CH_2CH_2\text{-}C \\ & & & | & & | \\ & & & C{\equiv}CH & & C{\equiv}CH \end{matrix} \right)$$
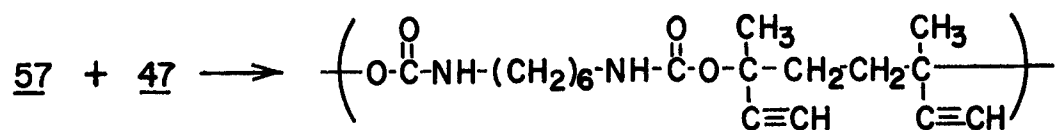
64

of 0.25 (0.50 g/dl in DMF at 25°C). The DSC thermogram of the polymer shows a baseline shift at 54°C followed by an exotherm beginning near 175°C with a maximum near 226°C followed by an endotherm with a minimum near 324°C (Figure 16). The TGA thermogram obtained in a nitrogen atmosphere shows that the exothermic process is accompanied by a 35 to 40% weight loss (Figure 17). An attempt to thermally cure the polymer at 200°C for 6 hr resulted in a 26% weight loss. The heat treated polymer was brown and leathery but not brittle. The DSC thermogram of this material shows only a large endotherm with a maximum near 338°C (Figure 16).

A sample of polymer 64 with an inherent viscosity of 0.40 (0.50 g/dl in DMF at 30°C) was obtained by allowing the monomers to initially react in sulfolane containing Nuocure^R 28. After 24 hr at 40°C, anhydrous DMF was added until the reaction mixture, which had slowly become cloudy, was completely clear. The polymerization was then allowed to proceed an additional 48 hr at 40°C.

Polyoxazolidone 65 was obtained from the polymerization of 57 and 47 in refluxing DMF containing triethylamine. The polymer, however, had an inherent

viscosity of only 0.07 (0.5 g/dl in DMF at 30°C). The DSC thermogram
shows baseline shifts near 70°C and 115°C (Figure 18). The TGA thermograms
obtained in air and argon atmospheres show initial weight losses near
225°C and 250°C, respectively (Figure 19).

$$\underline{57} \ + \ \underline{47} \rightarrow$$
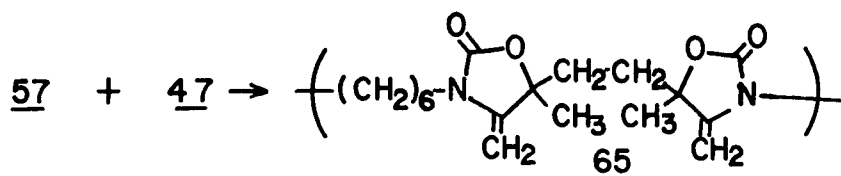
d. Intramolecular Cyclization of a Carbamate Model Compound

In order to determine the conditions necessary to convert alkynyl-
substituted polyurethanes to the corresponding polyoxazolidones, a study
of the base-catalyzed, intramolecular cyclization of a carbamate model compound
was carried out (TABLE 4). The conversion of a carbamate model compound (<u>55</u>)
to the corresponding oxazolidone (<u>56</u>) under various reaction conditions
was determined spectrophotometrically. Complete cyclization was attained
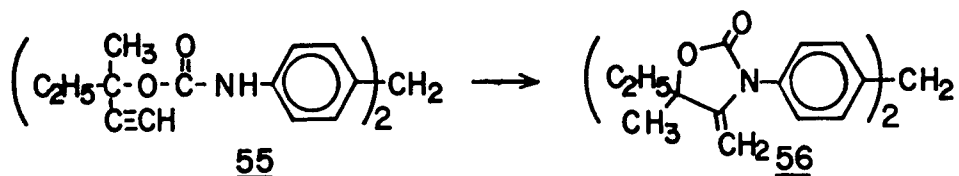
after 24 hr in heated NMP (60°C) containing sodium methoxide and in DMF
containing benzyltrimethylammonium hydroxide (Triton B). In the latter case,
cyclization occurred at ambient temperature and immediately upon the
addition of base.

e. Intramolecular Cyclization of Alkynyl-Substituted Polyurethanes

Solutions of polyurethanes <u>62</u> and <u>64</u> in DMF at ambient temperature
were treated with Triton B. In both cases, an almost instantaneous, quantitative
cyclization to the corresponding polyoxazolidone (<u>63</u> and <u>65</u>, respectively)
occurred. The infrared spectra and DSC thermograms of the polymers are
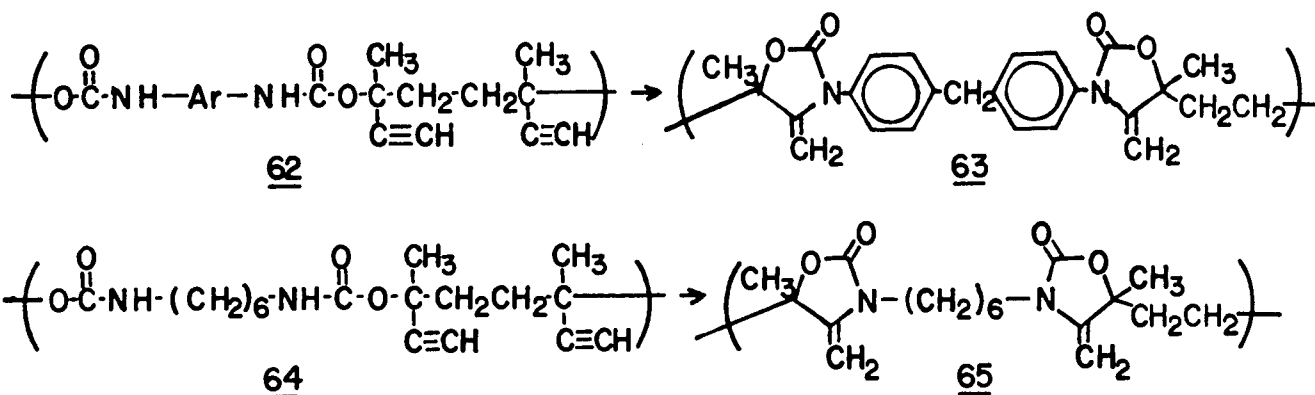
TABLE 4

INTRAMOLECULAR CYCLIZATION OF MODEL COMPOUND 55

Solvent	Base	Time/Temperature (hr/°C)	Degree of Cyclization[a] (%)
NMP	NaOMe	24/A[b]	40-50
NMP	NaOMe	2/75:24/A	50-60
NMP	NaOMe	24/60	100
DMF	Triton B[c]	0.25/A	100

a. Estimated from infrared spectrum of product.

b. Ambient temperature.

c. A 40% solution of benzyltrimethylammonium hydroxide in methanol.

TABLE 5

INTRAMOLECULAR CYCLIZATION OF ALKYNYL-SUBSTITUTED POLYURETHANES

Polyurethane Precursor	η_{inh}[a]	Tg(°C)	Polyoxazolidone	η_{inh}	Tg (°C)
62	0.31	130-135	63	0.16	170-175
64	0.40	50-55	65	0.31	70-75

a. Inherent viscosity (0.5 g/dl in DMF at 30°C).

identical to those of the polyoxazolidones prepared in one step. The increase in the chains' rigidities upon cyclization is reflected in the increase in Tg's (Table 5). Since the infrared spectra indicate that no hydrolysis occurred during the base treatment, the decreased viscosities must result from reductions in the polymers' end-to-end distances upon cyclization. The TGA thermograms of polyoxazolidone 65 indicate that the polymer prepared in two steps is slightly more thermally stable than the polymer previously prepared in one (Figure 20). The reduced thermal stability of the latter may be due to its very low molecular weight.

B. Transparent, Thermally-Stable Polymers

1. Aromatic Ionomers

The syntheses of polymers 66 and 68 (Polymers 16a and 18 in FINAL REPORT, Contract F33615-75-C-5073)[4] were scaled up to provide 35g of each material. The carboxylated polyphenylenes were then hydrolyzed in refluxing ethylene glycol containing potassium hydroxide to afford the corresponding aromatic ionomers 67 and 69. These samples were sent to the Air Force Materials Laboratory for physical testing.
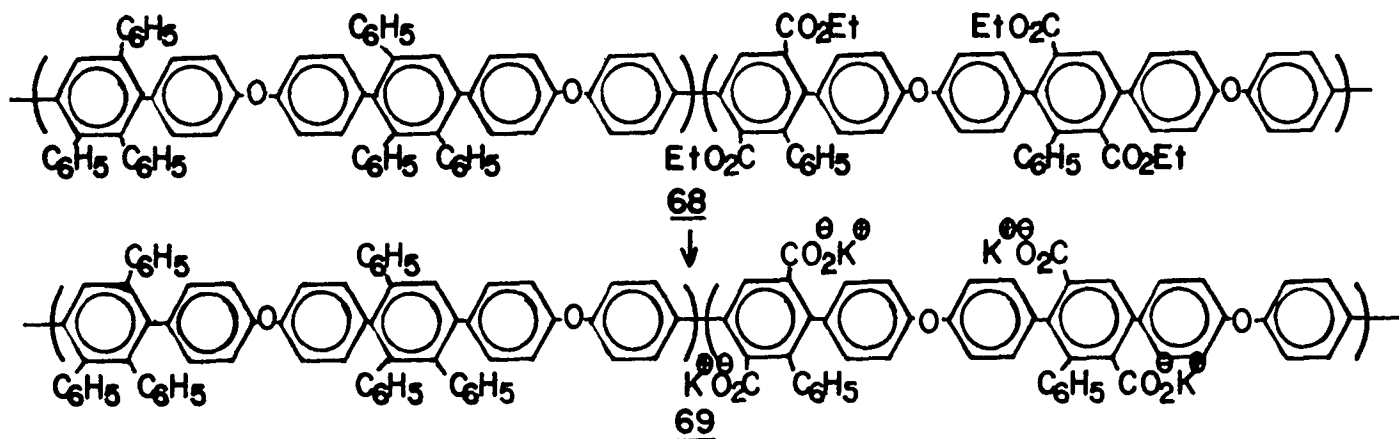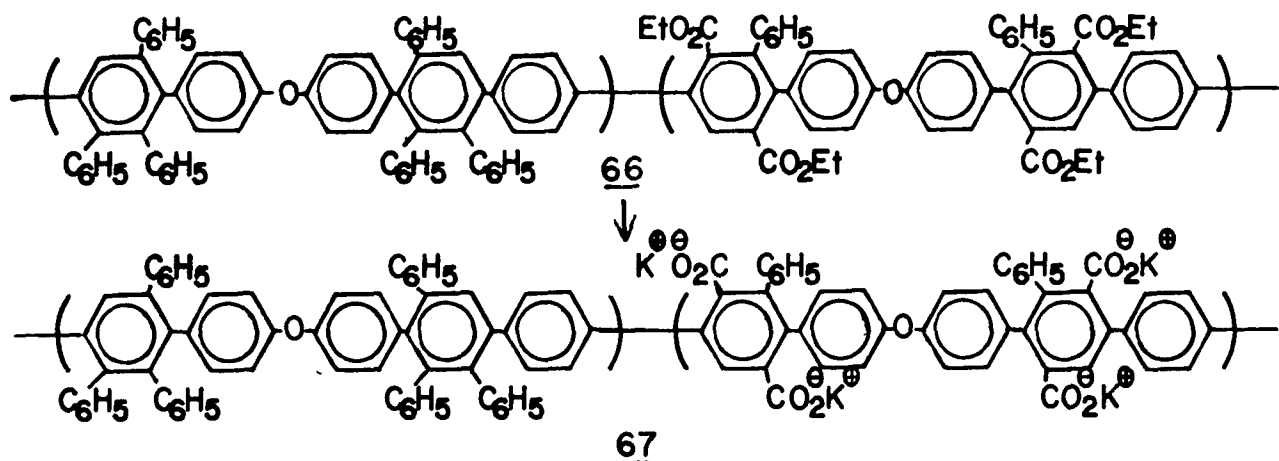
A sample of 66 was stirred in refluxing 1,4-butanediol containing potassium hydroxide. The infrared spectrum of the ionomer obtained shows that the pendent ester groups are completely hydrolyzed under these conditions. This is in contrast to the 70-85% hydrolyses obtained when the lower boiling ethylene glycol is used as the hydrolysis solvent. The completed hydrolyzed ionomer, however, is insoluble in common organic solvents.

In order to aid in the determination of conditions necessary to melt process aromatic ionomers, freeze dried samples of ionomer 67 were hot pressed at various temperatures (Table 6). The light-brown pellets, which are translucent, hard, and brittle, have densities that range from 0.971 to 1.046 g/cc. Maximum densities were obtained at 250°C under a pressure of 22,000 psi. Higher temperatures and extended heating cycles gave brittle pellets with lower densities. This may be due to oxidative crosslinking that occurs during the pressing procedure. This could be prevented by the use of more sophisticated melt-processing equipment.

A sample of ionomer 67 was stirred in refluxing concentrated hydrochloric acid to afford polymer 70. The pendent carboxylic acid groups were neutralized with barium acetate in refluxing ethylene glycol to yield the barium ionomer 71. The neutralization was followed by the disappearance of the acid carbonyl
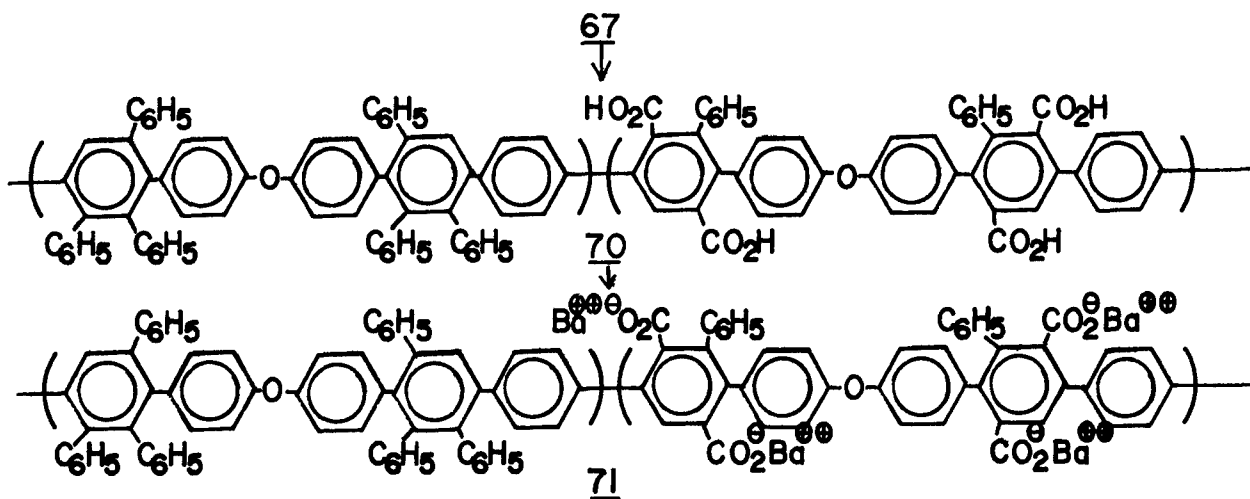
absortion shoulder at 1705 cm^{-1} in the ionomer's infrared spectrum. The polymer is soluble in hot dimethylsulfoxide (DMSO) and hot benzyl alcohol, in contrast to the insolubility displayed by previously prepared barium ionomers. The enhanced solubility is probably due to the polymer's lower crosslink density. Light-yellow, flexible, transparent films can be cast from hot solutions of either solvent. The TGA thermogram obtained in nitrogen shows an initial weight loss near 370°C (Figure 21).

Table 6. Effect of Temperature on the Hot Pressing of Polymer 67

Sample	Temperature[a] °C	Sample Wt Grams	Pellet Volume[bc] (cm^3)		Pellet Density[d] (g/cm^3)	
			#1	#2	#1	#2
1	28	0.1000	0.1030	0.1030	0.971	0.971
2	200	0.1000	0.0978	0.0978	1.022	1.022
3	250	0.1000	0.0959	0.0956	1.043	1.046
4	300	0.1000	0.0972	0.0978	1.029	1.022
5	340	0.1000	0.0975	0.0982	1.025	1.018

a. Samples preheated at specified temperature for 10 min.

b. $V = \pi r^2 h$ r = 0.635 cm.

c. gauge pressure = 22,000 lbs.

d. pellet wt./pellet vol.

24

2. Crosslinking of Phenylated Polyimides

a. New Diamine Monomers

The study aimed at the modification of phenylated polyimides to provide transparent, thermally-stable resins that can be crosslinked without the evolution of volatiles, which was initiated under U.S. Air Force Contract F33615-75-C-5073,[4] was continued with the synthesis of two new diamine monomers. Thus, diamine 73 was prepared by the reduction of 4-(2,4-dinitro-phenoxy) phenylacetylene (72), which was synthesized under the above contract.

$$O_2N-\bigcirc(NO_2)-O-\bigcirc-C\equiv CH \longrightarrow H_2N-\bigcirc(NH_2)-O-\bigcirc-C\equiv CH$$

$$\underline{72} \qquad\qquad\qquad \underline{73}$$
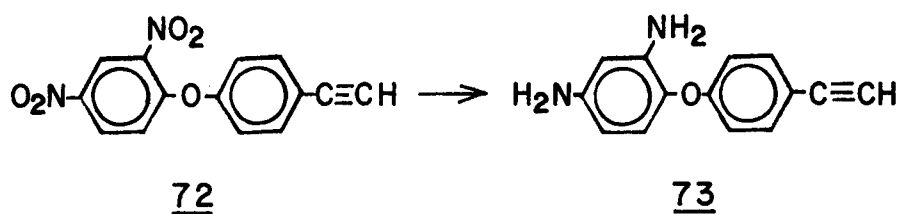
Initial attempts to reduce the compound 72 employing several different reducing agents failed to afford reasonable yields of the diamine 73. Reduction with sodium hydrosulfite did give a very low yield of a crude solid that displayed infrared absorptions characteristic of amines and alkynes. However, the crude product resisted purification. All attempts to isolate additional diamine from the reaction mixture were unsuccessful. The diamine 73 was obtained in 8% yield by the room temperature reduction of 72 with zinc and ammonium hydroxide.[30]

Since the trimethyl silane derivatives of ethynes are resistant to acids and hydrogenation,[31] the following synthetic scheme was attempted. Treatment of the dinitro compound 72 with butyl lithium followed by trimethylchlorosilane

$$\underline{72} \longrightarrow \underset{\underline{74}}{\overset{NO_2}{\underset{C\equiv C\text{-Si Me}_3}{\bigcirc(NO_2)-O-\bigcirc}}} \longrightarrow \underset{\underline{75}}{\overset{NH_2}{\underset{C\equiv CSi Me_3}{\bigcirc(NH_2)-O-\bigcirc}}} \longrightarrow \underline{73}$$
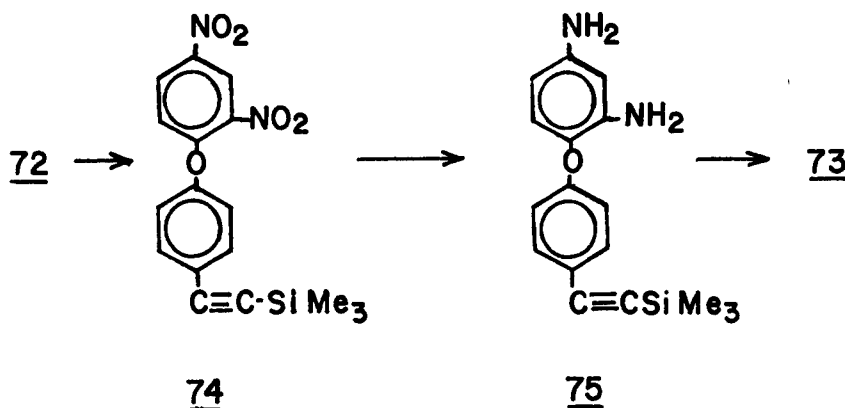
as described did not afford compound 74.[32]

The difficulty experienced in reducing the dinitrocompound 72 may be due to its base sensitivity. It has been reported that 2,4-dinitrodiphenyl ether reacts with sodium hydroxide.[33] Since almost all the chemical reductions of nitroacetylenes employ basic conditions, the following alternate route to the diamine 73 was investigated. The reaction of 2,4-diaminophenol dihydrochloride (76) with acetic anhydride followed by treatment with sodium methoxide gave the sodium salt 78. The coupling reaction of the phenol or its sodium salt with p-bromophenylacetylene (79a) or p-flurophenylacetylene (79b) under various experimental conditions did not afford compound 80.
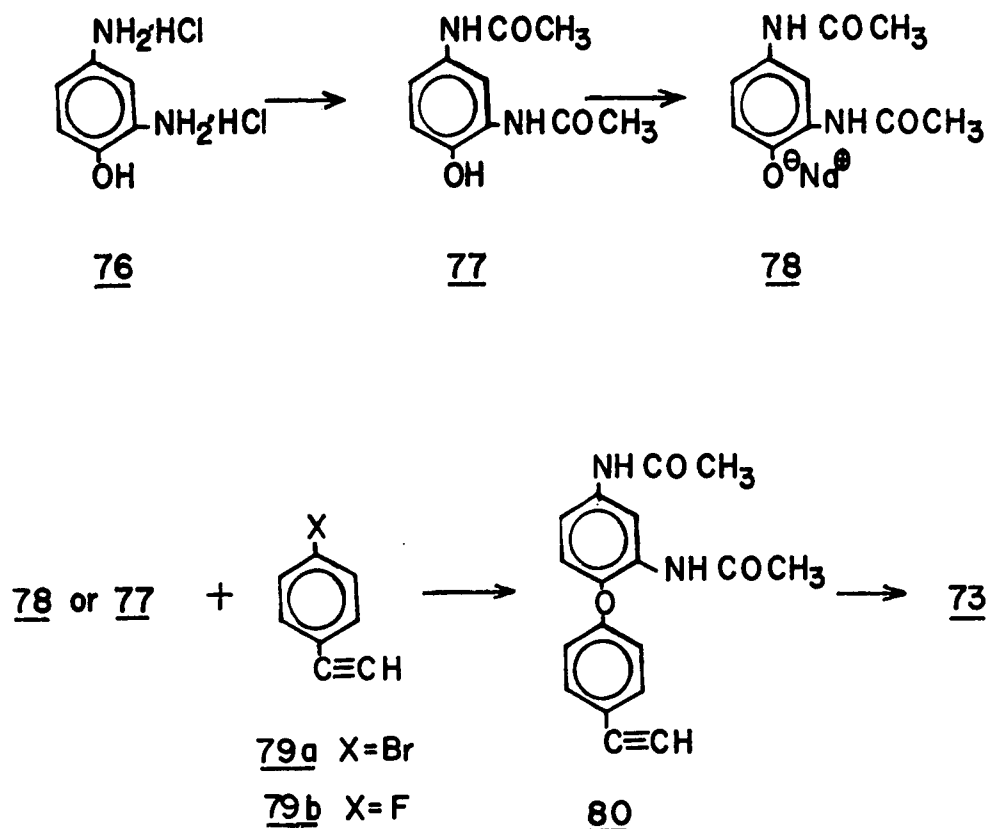
The synthesis of 73 via the following reaction scheme was also attempted. The reaction of 4-(2,4-dinitrophenoxy)acetophenone (81) with tin and hydrochloric acid gave the diamine 82. Treatment of 82 with a mixture of acetic acid and acetic anhydride gave the diacetamide 83. Reaction of 83 with a DMF/POCl$_3$ complex, however, failed to yield 84. Compound 83 was also allowed to react with PCl$_5$, however, no product could be isolated from the reaction mixture.

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81 → **82** → **83** ↛
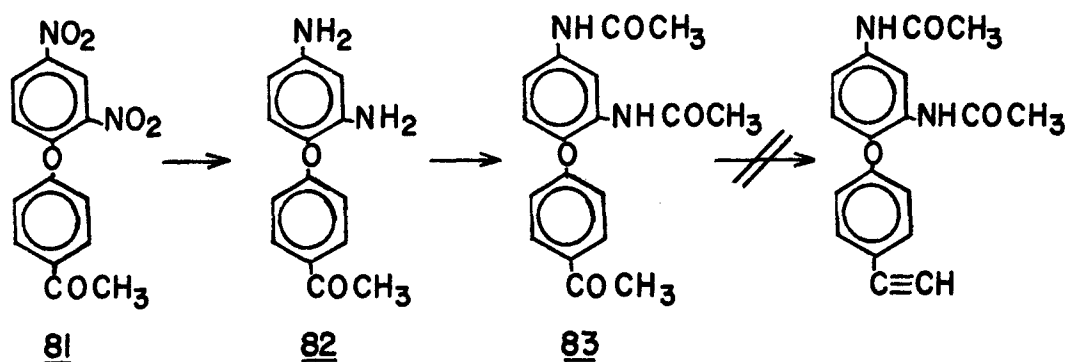
The synthesis of another ethynyl-substituted aromatic diamine (91) was then investigated. Silane 87 was prepared from p-bromoacetophenone (85) according to the known procedure.[34] The reaction of 87 with magnesium in THF gave the corresponding Grignard reagent 88,[35] which was converted to the organo cadmium compound 89. Treatment of 89 with 3,5-dinitrobenzoyl chloride, however, did not afford compound 90.

85 → **86** → **87** → **88** → **89**

89 + → **90** → **91**
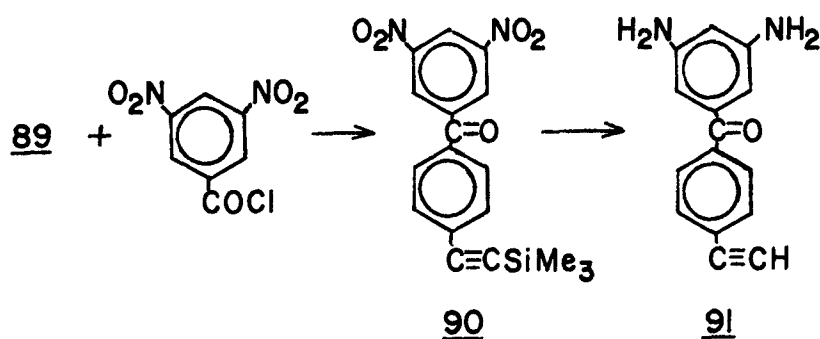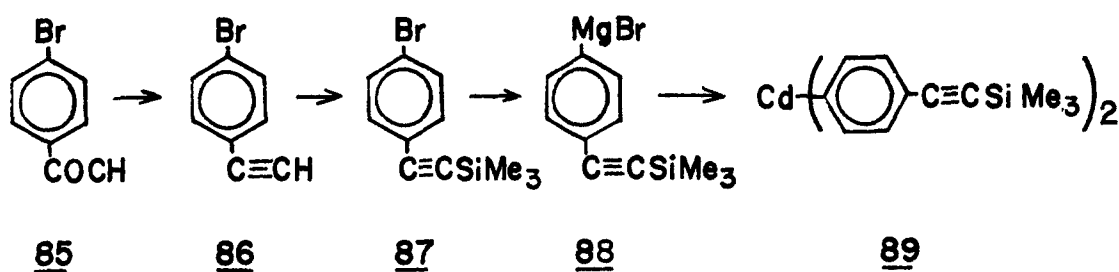
The preparation of a second monomer, i.e., 3,5-diaminodiphenylacetylene (96), was accomplished with a new synthetic sequence. Previous attempts to prepare this monomer via the reduction of 3,5-dinitrophenylacetylene had been unsuccessful.[4] Hence, an alternate route was devised in which the nitro groups were reduced early in the sequence. Thus, treatment of 3,5-dinitroiodo-benzene (92) with a tin/hydrochloric acid reagent[48] afforded 3,5-diaminoiodo-benzene. Since the compound darkened immediately on exposure to light, it

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was isolated as the hydrochloride 93. The reaction of 93 with acetic
anhydride and sodium acetate gave the acetylated diamine 94, which was
coupled with cuprous phenylacetylide in HMPA to yield the adduct 95.
In an alternate procedure, the hydrochloride 93 was not isolated, but was
converted to the acetylated diamine 94 in situ. Hydrolysis of 95 with
potassium hydroxide in ethanol afforded the diamine 96. The product, which
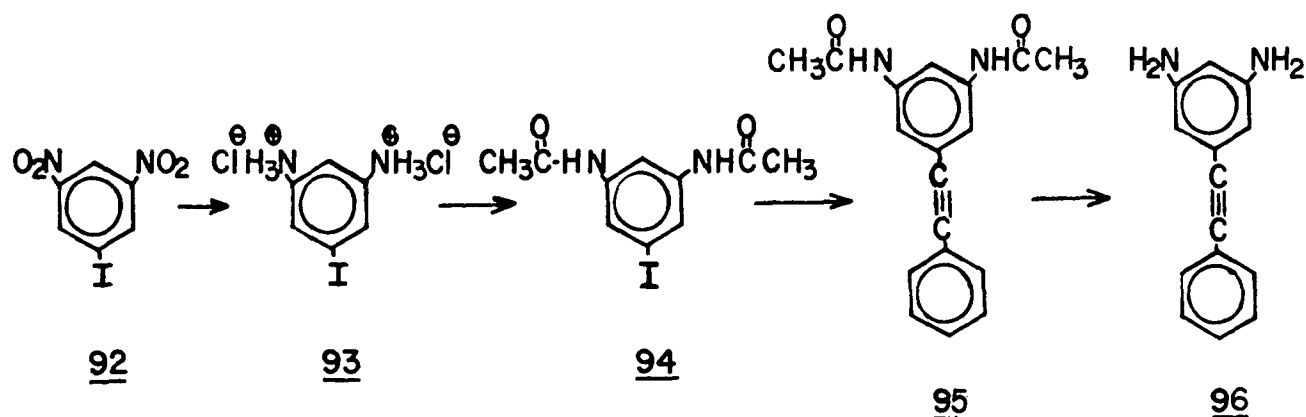
was recrystallized from benzene did not display an ethynyl absorption in its
IR spectrum. This behavior, however, is not surprising since it is
known that the ethynyl group absorption is either weak or absent for
disubstituted acetylenes. The mass spectral spectrum of the white crystalline
compound is in accordance with the proposed structure. The amino protons at
3.35 ppm in the NMR spectrum were found to be exchangeable with deuterium
oxide. Surprisingly, the diamine shows no tendency to undergo oxidation when
stored in the solid state. Solutions of 96, however, do darken after several
days when exposed to air.

b. Polyimide Model Compound

In order to determine the optimum conditions for the polymerization of
96 with phenylated dianhydrides, the model reaction of the diamine with
tetraphenylphthalic anhydride (97) was investigated. This reaction in
m-cresol containing isoquinoline [36] afforded a quantitative yield of the model
compound 98. As in the case of the diamine, the IR spectrum of 98 did not

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show ethynyl absorptions. The presence of the ethynyl group was substantiated by preparing a hydrogenated derivative. Thus, hydrogenation of 98 in the presence of a Raney Nickel catalyst afforded compound 99. Elemental and NMR analysis confirmed the structure of the hydrogenated product.
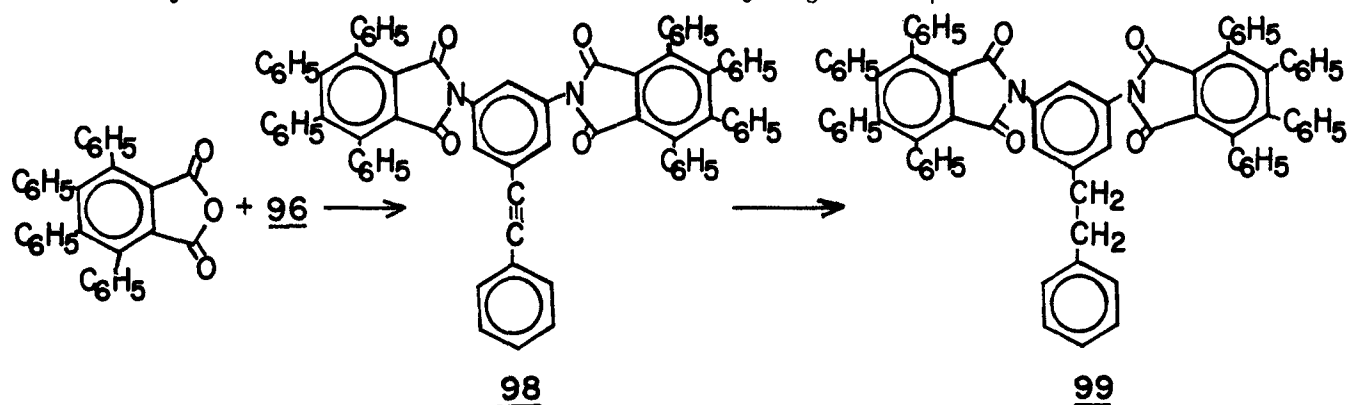
The DSC thermogram of 98 shows an endotherm due to melting near 400°C followed by a sharp exotherm at 425°C (Figure 22). This exotherm can be attributed to the thermal polymerization of the ethynyl group. The TGA thermogram in air shows a major weight loss beginning near 450°C (Figure 23).

c. Polymerization of Alkynyl-Substituted Diamines

The initial polymerization of diamine 73 with phenylated dianhydride 100 in refluxing m-cresol containing isoquinoline resulted in an insoluble, cross-linked polymer. Therefore, the polymerization was carried out at a lower temperature by employing a m-cresol/benzene solvent system. In this case a polymer was obtained (101) that is soluble in chlorinated hydrocarbons and has an inherent viscosity of 0.18 (0.25 g/dl in sym-tetrachloroethane at 30°C). The polyimide can be cast into thin, clear, slightly-yellow,brittle films. The
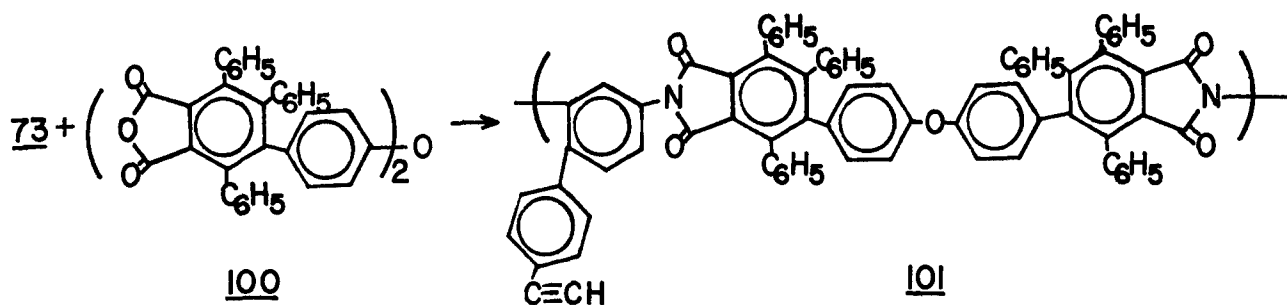
DSC thermogram shows a strong exotherm near 250°C, which is indicative of the polymerization of the pendent ethynyl groups (Figure 24). The infrared spectrum shows a strong absorption near 3300 cm,$^{-1}$ characteristic of ethynyl groups. The TGA thermogram of the uncured polymer shows an initial weight loss in air near 400°C (Figure 25). The slow heating of a sample of 101 to 225°C for 4 hr resulted in a completely insoluble material. The time required for crosslinking was dependent on the temperature. Lower temperatures required longer reaction times. Thus, completely insoluble material was also obtained by heating the polymer for 3 hr at 250°C, for 6 hr at 210°C,or for 24 hr at 190°C. The DSC thermogram of the cured polymer shows no exotherm (Figure 24). The TGA thermogram of the cured polymer shows no weight loss in air before 400°C (Figure 25).

The polymerization of diamine 96 with 100 was then carried out in refluxing m-cresol containing isoquinoline. The polyimide 102, which was obtained in almost quantitative yield, is soluble in common organic solvents,
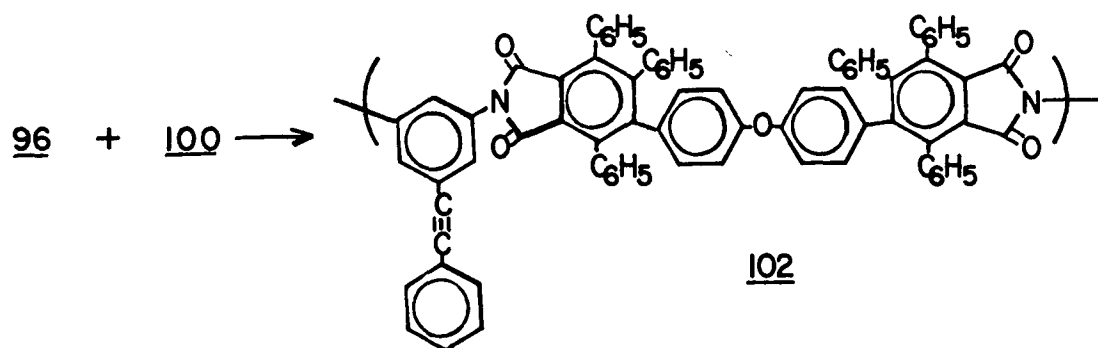
such as, benzene, chloroform etc., and has an inherent viscosity of 0.67 (0.250 g/dl in sym-tetrachloroethane at 30°). The TMA thermogram obtained with a penetration mode shows a Tg near 355°C (average value of the highest penetration rate at T=20°/min, 10g load). The TGA thermogram indicates that the polymer is stable to near 500°C in nitrogen,and 400°C in air (Figure 26). The broad exotherm with a maximum near 450°C in the DSC thermogram can be attributed to the thermal polymerization of the pendent ethynyl substituents (Figure 27). Crosslinking could also be affected by heating the polymer under vacuum at 350°C for 4 hr.

d. Polyimide Copolymers

In an attempt to lower the crosslink density in the phenylated polyimide resins, two copolymerizations of dianhydride 100 with diamine 96 and 4,4'-diaminodiphenyl ether (103) were carried out. Molar ratios of 100: 96: 103 of 10:1:9 and 10:2:8 were employed. In both cases, the copolymer obtained did undergo crosslinking at 350°C. The copolymers' properties were similar to those of the homopolymer.

The use of relatively inexpensive dianhydride was investigated in the polymerization of benzophenone 3,3',4,4'-tetracarboxylic dianhydride with 96 and 103. A molar ratio of 10:2:8 was employed. The copolymer, however, crosslinked during the polymerization.

e. Attempted Use of a Reactive Plasticizer

In an attempt to lower the temperature needed for crosslinking of the pendent phenylethynyl substituents, the use of a reactive plasticizer was investigated. Reactive plasticizers have been used to lower the temperature needed to process a polymer and then, in effect, removed by their thermal polymerization. A primary criteria for their use is compatibility with the polymer. Plastizers and polymers with similar structures usually afford the most compatible systems. Hence, compound 105 was prepared by the reaction of m-ethynylaniline (104) with 3,4,5,6-tetraphenylphthalic anhydride (97). This compound was expected to be compatible with the phenylated polyimides and
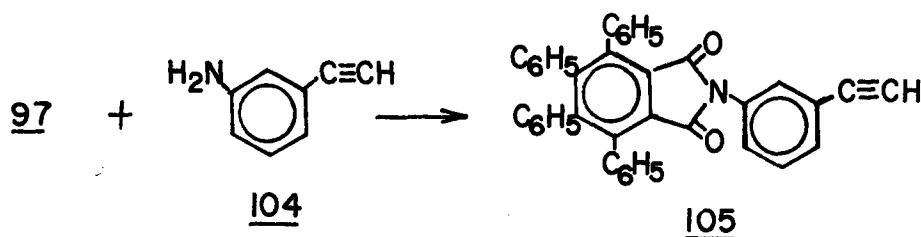
undergo thermal polymerization near 250°C. It was also hoped that the polymerization of the ethynyl compound in the presence of polymer 102 would result in the copolymerization of the respective ethynyl and phenylethynyl substituents. The DSC thermogram of compound 105 does show a strong exotherm near 270°C (Figure 28). The TGA thermogram in nitrogen shows no weight loss until near 400°C (Figure 29). These results are consistant with an exothermic polymerization of the ethynyl substituent.

Two mixtures of the plasticizer and polymer 102 were prepared by dissolving both components in chloroform, stirring, and then removing the solvent under reduced pressure. The solid mixtures, which contained 10 and 20% plasticizer, were heated at 225°C for 4 hr under vacuum. The polymer, however, was still soluble in organic solvents after the heat treatment indicating that crosslinking did not occur. The DSC thermogram of the 10% mixtures did not show an exotherm near 270°C. The plasticizer did lower the T_g of the polymer. The 10 and 20% mixtures displayed the T_g's of 327°C and 320°C, respectively (average values of the highest penetration rate on TMA at $\Delta T = 20°C/min$, 10 g load).

SECTION III
EXPERIMENTAL

A. Physical Determinations

Infrared spectra were obtained on Perkin Elmer Model 457 and Model 621 spectrophotometers. Proton NMR spectra were obtained with a Varian HA-60-IL NMR spectrometer. All samples were run at concentrations of 10-20% using tetramethylsilane as an internal standard. Elemental analyses were performed by Midwest Microlab, Indianapolis, Indiana. DSC spectra were obtained on a Dupont 900 Thermal Analyzer with a heating rate of 10°C/min. Thermogravimetric analyses were carried out on a DuPont 951 Thermogravimetric Analyzer with a heating rate of 5°C/min. Inherent viscosities were measured in a Cannon-Ubbeholde Microdilution Viscometer No. 75. Several glass transition temperatures were determined by Dr. G. H. Ehlers at AFML, WPAFB. The values reported were obtained by correlating DSC and TMA data.

B. Preparation of New Adhesive Systems

1. Preparation of unsaturated polyester resin 3:[5]

A 1 ℓ four-necked round bottom flask fitted with a mechanical stirrer, nitrogen inlet, pyrometer and deanstark trap was charged with 35 ml of decalin, 98.06 g (1 mol) of maleic anhydride, and 31.04 g (0.5 mol) of ethylene glycol. The reaction mixture was heated to 105°C at which time 31.04 g (0.5 mol) of additional ethylene glycol, 0.17 g (1 mmol) of p-toluenesulfonic acid and 0.1 g of hydroquinone were added. The resulting solution was heated to reflux for 2 hr during which time 99% of the theoretical amount of water was collected. The resin mixture was then cooled slightly and poured into a heavy-walled glass jar. The decalin polyester mixture separated upon cooling to room temperature.

2. Attempted reaction of 2,3-dimethyl-1,3-butadiene with diethyl maleate

A mixture of 2.0 g (11.6 mmol) of diethyl maleate and 1.05 g (12.8 mmol) of 2,3-dimethyl-1,3-butadiene were allowed to stand at room temperature for 24 hr. The excess dimethyl butadiene was removed under reduced pressure (10 mm) at room temperature. The residue was fractionally distilled under reduced pressure to yield 1.7 g (85% recovery) of diethyl maleate.

3. Attempted reaction of furan with diethyl maleate

A mixture of 2.0 g (11.6 mmol) of diethyl maleate and 0.87 g (12.8 mmol) of furan were allowed to react under the conditions described above. The workup procedure as described above yielded 1.6 g (80% recovery) of diethyl maleate.

4. Attempted cure of unsaturated polyester resin 3

A 1.0 g sample of polyester resin 3 was mixed thoroughly with 2 g of 2,3-dimethyl-1,3-butadiene. The ester-diene mixture was placed in a closed flask and kept in the dark for 48 hr. Upon examination of resin, no signs of reaction were observed. The solubility and viscosity of the polymer were essentially unchanged. Similar tests carried out using furan as the curing agent, produced analogous results.

5. Benzonitrile oxide (9)

This compound was generated in situ by the treatment of benzhydroxamoyl chloride [37] with triethylamine in acetone.[38]

6. Reaction of 2-butyne-1,4-diol with benzonitrile oxide

To a solution of 1.0 g (11.6 mmol) of 2-butyne-1,4-diol and 1.8 g (11.6 mmol) of benzhydroxamoyl chloride in 15 ml dry acetone was added dropwise 1.2 g (11.8 mmol) of triethylamine. An exothermic reaction took place with the formation of a precipitate. The reaction mixture was stirred for 3 hr and then filtered. The acetone was removed under reduced pressure and the resulting oil cooled until crystallization appeared complete. The resulting brown oily solid was isolated in 50% yield: ir (neat 3300 (s, O-H), 3050 (s,ϕ-H), 1590 cm^{-1} (s, olefinic bonds of isoxazole).

7. Acetylenic polyester 13

The polyester was prepared by the reaction of 2-butyne-1,4-diol with phthalic anhydride according to the known procedure.[6]

8. Reaction of benzonitrile oxide with polyester 13

The procedure is essentially that described above except 1.0 g of acetylenic polyester was used instead of the 2-butyne-1,4-diol and the reaction mixture was allowed to stir overnight. The acetone was removed under reduced pressure to yield a light brown rubbery solid: ir (film from CHCl$_3$) 1725 (s,C=O), 3400 (w, OH end groups).

9. Polymerization of furfuryl alcohol

A mixture of 100.0 g of furfuryl alcohol and 0.5 g 85% phosphoric acid dissolved in 10 ml of water was heated to 105°C for 90 min according to the known procedure.[7] The reaction mixture was cooled, and neutralized to pH 5 with 10% sodium hydroxide. After neutralization, the mixture was heated under reduced pressure and 85% of the theoretical amount of water was removed by distillation. The resulting resin was dried at room temperature under reduced pressure for 48 hr to afford a 90% yield of dehydrated product.

10. Addition of diethyl azodicarboxylate to resin 16

Treatment of 2.0 g of the furyl resin <u>16</u> with 2 g of diethyl
azodicarboxylate resulted in an immediate temperature rise of 80°C. When
the reaction mixture was cooled to ambient temperature it rapidly solidified;
ir (CHCl$_3$) 1720 cm^{-1} (s, C=O).

11. Addition of 4-phenyl-1,2,4-triazoline-3,5-dione to resin 16

A solution of 0.9 of 4-phenyl-1,2,4-triazoline-3,5-dione in 8 ml
of acetone was added to 1.0 g of the alkylfuryl resin and the two components
mixed thoroughly. The reaction mixture solidified immediately. The brittle
red solid was broken up and dried under high vacuum for 18 hr.

12. Reaction of dimethylfuran with maleic anhydride

This model compound was prepared according to the known procedure[9]
in 85% yield: mp 76.5-77.5°C (lit.[9] mp 78°C).

13. Addition of maleic anhydride to resin 16

Equal weights of the alkyl-furyl resin <u>16</u> and finely powdered maleic
anhydride were stirred together for 5 min. The maleic anhydride appeared to
be soluble in the resin. After the reactants were thoroughly mixed, the reaction
mixture was allowed to stand overnight at ambient temperature. The resulting
solid was broken up and dried at ambient temperature under vacuum for 24 hr.
The above reaction was also carried out using 30 ml of chloroform as the
solvent. The polymer was precipitated in 300 ml of diethylether, and reprecipi-
tated from acetone with ether.

14. Phenyl propioloamide (23)

The amide was prepared in 84% yield by the known procedure[10]
mp 106-107°C (lit [10] 106°C).

15. Phenyl propiolonitrile (24)

Treatment of phenyl propiloamide with P$_2$O$_5$ in paraffin oil as
described [11] afforded the nitrile in 77% yield: bp 91-92°C (8 mm) [lit [10]
105-106°C (13 nm)]; ir (CCl$_4$) 2270 (s, C≡C) and 2147 cm^{-1} (m, C≡N).

16. Acetylenedicarboxamide (26)

This compound was prepared according to the known procedure [12] in
90% yield: mp 190°-192°C (lit [12] 190-192°C).

17. Dicyanoacetylene (27)

Numerous attempts to prepare this compound by dehydration of
acetylenedicarboxamide with P$_2$O$_5$ according to the known procedures resulted
in small amounts of impure product.[11,13] Changes in both reaction time
and temperature resulted in only slight improvements in purity and yield. The

dinitrile was prepared in 25-35% yield by the dehydration of the diamide using polyphosphate ester (PPE) according to the following procedure: A suspension of 6.0 g (0.053 mol) of acetylenedicarboxamide in 50 g PPE was degassed for 15 min with nitrogen. As the temperature of the reaction mixture was raised to 170-180°C, the nitrile began to distill into the receiver cooled in a dry ice-acetone bath. The heating was continued for 30 min to afford 1.3 g (32%) of product:[14,15] ir (CCl$_4$) 2240 (m, C≡N), 2259 cm^{-1} (2, C≡C).

18. <u>Attempted cure of alkylfuryl resin 16 with phenylpropiolonitrile</u>

Equal parts by weight of resin 16 and phenylpropiolonitrile were mixed thoroughly and allowed to stand at ambient temperature for 48 hr. No changes in the physical state of the resin were observed.

19. <u>Attempted cure of alkylfuryl resin 16 with dicyanoacetylene</u>

Equal parts by weight of resin <u>16</u> and dicyanoacetylene were mixed thoroughly and allowed to stand at ambient temperature for 48 hr. No changes in the physical state of the resin were observed.

20. <u>Poly(phenylacetylene)(29)</u>

A 10% (V/V) solution of phenylacetylene in toluene was placed in a glass ampule. After 0.5% azo-bis-isobutyronitrile (AIBN) was added, the ampule was attached to a high vacuum system, degassed and sealed. It was then heated at 50°C for 3 days. The solvent and unreacted monomer were removed under reduced pressure to afford a 30% yield of the liquid polymer.[16]

21. <u>Attempted addition of dienophiles to polyphenylacetylene</u>

Equal parts by weight of polyphenylacetylene and the dienophile, i.e., maleic anhydride, tetracyanoethylene, or phenylacetylene, were stirred at ambient temperature for 48 hr. However, no reaction occurred under these conditions.

22. <u>Phenyl vinyl ether (36)</u>

The compound was prepared in 60% yield from phenol according to the known procedure:[21] bp 45-47°C (10 mm) [lit [21] to°C (12 mm)].

23. <u>1,2-Dibromo-1-phenoxyethane (37)</u>

To a solution of 10 g (0.083 mol) of phenyl vinyl ether in diethyl ether at 0°C was added 13.3 g of bromine. The addition was controlled so that the temperature remained constant. The diethyl ether was removed under reduced pressure and the remaining liquid fractionally distilled to give 20.0 g (86%) of the colorless liquid: bp 124-125°C (11 mm).[22]

24. Phenoxyacetylene (38)

Procedure 1

A mixture of 10 g (35.7 mmol) of 1,2-dibromo-1-phenoxyethane and 59 g powdered 85% KOH contained in a distillation apparatus were slowly heated under reduced pressure (10 mm). The temperature was increased slowly to 100°C, at which time phenoxyacetylene and water began to distill rapidly. After the distillation was complete (20 min), the distillate was dissolved in ether, dried over potassium carbonate, and fractionally distilled to give 0.5 g (12%) of phenoxyacetylene: bp 46-48°C (10 mm) [lit [22] 43-44°C (10 mm)].

Procedure 2

To a stirred solution of 0.5 g sodium in 150 ml of liquid ammonia was added 2.0 g of ferric chloride. After an additional 6.0 g of sodium was added, the mixture was stirred for 1 hr. 1,2-Dibromo-1-phenoxyacetylene (27.4 g, 0.10 mol) was then added over a period of 45 min. The ammonia was allowed to evaporate overnight. To the resulting dark-brown residue was added 200 ml of ether followed by 200 ml of water. After the mixture was stirred for 5 min, the organic layer was separated, washed twice with 200 ml portions of water, and dried over anhydrous sodium sulfate. The ether was removed under reduced pressure, and the residue distilled to yield 6.0 g (52%) of phenoxyacetylene: bp 34-35°C (5 mm); ir (CCl_4) 3342 (s-C≡C-H) and 2209 cm^{-1} (s,-C≡C-).

25. Bis(benzonitrile)palladium chloride

The compound was prepared in 90% yield according to the known procedure.[39]

26. Poly(phenoxyacetylene) (31)

To a solution of 0.5 g (4.2 mmol) of phenoxyacetylene in 5 ml benzene was added 1 drop of a 0.10% solution of bis(benzonitrile) palladium chloride in benzene. The resulting black-brown mixture was allowed to stand at room temperature for four days after which time an additional 5 ml of benzene was added and the mixture filtered. The red-brown solid (0.4 g) was washed with methanol and air dried.[19]

27. Reaction of phenylacetylene with poly(phenoxyacetylene)

A mixture of 0.3 g of poly(phenoxyacetylene) and 5 ml of phenylacetylene was stirred at ambient temperature for 24 hr. Since no reaction occurred, the mixture was dissolved in 10 ml of bromobenzene, and the resulting solution

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heated at reflux for 16 hr. The solution was added to petroleum ether to afford a light-brown precipitate.

28. General procedure for the polymerization of diepoxides and diisocyanates

Eqimolar amounts of 2,2-bis[4-(2,3-epoxypropoxy)phenyl]propane and toluene-2,4-diisocyanate were mixed with 1% catalyst (w/w) and allowed to stand at room temperature. The mixture was manually stirred periodically, and the viscosity of the solution noted.

29. 3,6-Dihydroxy-3,6-dimethyl-1,7-octadiyne (47)

The bisalkynol was prepared by a modification of the previously described procedure.[29] To a solution of 2.0 g of metallic sodium in 750 ml of liquid ammonia was slowly added 0.2 g of ferric nitrate. After the brisk evolution of hydrogen ceased, 18.7 g of additional sodium was slowly added. The solution was then saturated with dry acetylene gas. Acetonylacetone (43.0 g) was added dropwise over a period of 15 min under a constant acetylene pressure. The resulting mixture was allowed to reflux under acetylene for 35 hr. The condensor was removed and the ammonia allowed to evaporate overnight. Ice water was slowly added to the solid residue, and the pH of the resulting solution adjusted to 2 with dilute tartaric acid (165 g in 250 ml H_2O). The solution was then extracted with 3 150-ml portions of ether. The extracts were combined, washed with saturated sodium chloride, dried over anhydrous magnesium sulfate, and evaporated to dryness. The residue was recrystallized from heptane to afford white crystals, mp 91.5-92.5°C (lit [29] 92-92.5). The monomer was sublimed twice under reduced pressure immediately prior to use.

30. Reaction of TDI with 3-methyl-1-pentyn-3-ol

Procedure 1

To a solution of 19.6 g (0.20 mol) of 3-methyl-1-pentyn-3-ol in 50 ml of anhydrous NMP was slowly added 17.4 g (0.10 mol) of TDI. The addition was carried out over a period of 1 1/2 hr in order to maintain the temperature between 25 and 30°C. The reaction mixture was stirred for 4 hr at ambient temperature and then added to 200 g of crushed ice. The infrared spectrum of the white polymeric precipitate that formed contained absorptions characteristic of a urea (1640 cm^{-1}). This product probably resulted from the reaction of unreacted TDI with water.

Procedure 2

Procedure 1 was repeated using anhydrous DMF as the solvent. In this case, the reaction mixture was stirred for 36 hr at ambient temperature at which time the solution solidified to afford a yellow, insoluble gel: ir (KBr)

3330 (W,≡C-H), 1720 (S,-O-CO-NH-) and 1660 cm^{-1} (S,-NH-CO-NH-).

Procedure 3

Procedure 1 was repeated in toluene containing 3 ml of triethylamine.
The reaction mixture was stirred at ambient temperature for 24 hr and then
added to hexane. The precipitate that formed was recrystallized from a
benzene-heptane mixture to afford a tan powder: mp 165-168°C (d); ir (KBr)
3300 (W,≡C-H), and 1730 cm^{-1} (s,-O-CO-NH-).

31. <u>3,3'-(2-Methyl-p-phenylene)bis(5-methyl-5-ethyl-4-methylene-2-oxazolidone)</u>
   <u>(50)</u>

Procedure 1

A solution of 3.83 g (0.022 mol) of TDI in 10 ml of cyclohexane was
slowly added to a solution of 4.32 g (0.044 mol) of 3-methyl-1-pentyn-3-ol
and 0.005 g sodium methoxide in 40 ml of cyclohexane. The mixture was
stirred at ambient temperature for 12 hr, and then added to 200 ml of ice
water containing 10 drops of conc H$_2$SO$_4$. The precipitate that formed was taken
up in ether. The ether solution was dried over sodium sulfate, and the
ether removed under reduced pressure to afford a brown, waxy solid. Attempts
to purify this product were unsuccessful. The infrared spectrum showed
oxazolidone (s,1760 cm^{-1}) and carbamate (s, 1730^{-1}) absorptions.

Procedure 2

Procedure 1 was repeated with anhydrous NMP as the solvent. The
reaction was allowed to proceed for 24 hr at ambient temperature to give
a crude product that resisted purification. The reaction was also run at
100°C for 14 hr to afford a brown product that could not be purified.
The infrared spectra of the products showed oxazolidone and carbamate
absorptions.

Procedure 3

A solution of 8.700 g (0.05 mol) of TDI in 10 ml of toluene was
slowly added to a solution of 9.8050 g (0.10 mol) of 3-methyl-1-pentyn-3-ol
and 1 ml of triethylamine in 20 ml of toluene. The mixture was heated at
reflux for 24 hr and then allowed to cool. The precipitate that formed was
collected by filtration and recrystallized from toluene to yield 14.0679 g
(76%) of a white powder: mp; 168.5-169.5°C; ir (IBr) 1755 (s, oxazolidone
C=O), 1675, 1635, and 810 cm^{-1} (m,m,w, C-CH$_2$); nmr(CDCl$_3$) δ 7.40 (m,6H,C$_6$H$_3$),
3.08 (m,4H,=CH$_2$), 2.06 (m,2H,-CH$_2$-), 1.56 (s,6H,-CH$_3$) and 1.00 ppm (t,6H,-CH$_3$).
<u>Anal.</u> Calcd for C$_{21}$H$_{26}$N$_2$O$_4$: C,68.08; H,7.08; N,7.56
Found: C,68.31; H,7.24; N,7.36

32. <u>Reaction of phenyl isocyanate with 3,6-dihydroxy-3,6-dimethyl-1,7-octadiyne</u>

<u>Procedure 1</u>

A solution of 2.6835 g (0.0225 mol) of phenyl isocyanate in 20 ml of anhydrous NMP was slowly added to a solution of 1.8562 g (0.0112 mol) of 3,6-dihydroxy-3,6-dimethyl-1,7-octadiyne in 30 ml of NMP. The addition was carried out over a period of 2 hr while the temperature of the reaction was maintained at 25-30°C. The mixture was stirred an additional 4 hr at ambient temperature and then poured into ice water. The precipitate that formed was collected by filtration and recrystallized from ethanol to afford white crystals: mp 240-242°C; ir (KBr) 1640 cm^{-1} (-NH-CO-NH-). (Product is N,N'-diphenylurea which evidently resulted from the reaction of unreacted phenyl isocyanate with water.)

<u>Procedure 2</u>

Procedure 1 was repeated with the reaction mixture being heated at 100°C for 14 hr. The addition of the mixture to water again resulted in the isolation of N,N'-diphenylurea.

<u>Procedure 3</u>

Procedure 1 was repeated using anhydrous DMF as the solvent. After the reaction mixture was stirred under nitrogen at ambient temperature for 48 hr, a portion of the solution was removed and added to crushed ice. The infrared spectrum of the crude product contained isocyanate absorptions indicating incomplete reaction. Hence, the remaining reaction mixture was heated at 70°C for 24 hr and then added to crushed ice. The infrared spectrum of the crude product showed absorptions characteristic of urethane, oxazolidone, and urea moieties.

<u>Procedure 4</u>

A solution of 2.1 g (0.018 mol) of phenyl isocyanate in 10 ml of toluene was slowly added to a solution of 1.5 g (0.009 mol) of 3,6-dihydroxy-3,6-dimethyl-1,7-octadiyne and 3 ml of triethylamine in 30 ml of toluene. The mixture was stirred overnight at ambient temperature during which time a white precipitate formed. The infrared spectrum of the crude product contained absorptions characteristic of both carbamate and oxazolidone moieties. The product was recrystallized twice from toluene to give a 50% yield of white needles: mp 231-233°C; ir (KBr) 3250 (s,≡C-H), 2070(w,-C≡C-) 1700 and 1720 cm^{-1} (s,-O-CO-NH-).

Procedure 5

Procedure 4 was repeated using anhydrous DMF as the solvent. In this case, the mixture was stirred under vacuum at ambient temperature for 24 hr and then added to crushed ice. The infrared spectrum of the crude product showed absorptions characteristic of urethane, oxazolidone, and urea moieties.

Procedure 6

Procedure 5 was repeated with freshly sublimed DABCO being used in place of triethylamine. The mixture was stirred for 24 hr at ambient temperature and then added to ice water. The white solid that precipitated was recrystallized from toluene to give a white powder: mp 187-189°C; ir (KBr) 3250 (s,$\equiv$C-H), 2090 (w,-C$\equiv$C-), 1700 (s,-O-CO-NH-), 1640 (m,-NH-CO-NH) and 1600 cm^{-1} (s, aromatic).

Anal. Calcd for $C_{24}H_{24}N_2O_4$: C, 71.27; H, 5.98; N, 6.93
Found: C, 72.03; H, 5.96; N, 8.85

Procedure 7

To a solution of 1.2121 g (0.007 mol) of 3,6-dihydroxy-3,6-dimethyl-1,7-octadiyne and 3 drops of Nuocure^R 28 (0.03 g) in 15 ml of anhydrous DMF was slowly added 1.6943 g (0.014 mol) of phenyl isocyanate in 10 ml of anhydrous DMF. After the addition, which was carried out under nitrogen, was complete, the mixture was stirred under nitrogen at ambient temperature for 16 hr. During this time a small amount of white solid precipitated from solution. The reaction mixture was added to crushed ice to afford 2.6 g (90%) of crude product. The white solid was recrystallized from toluene to give white needles: mp 232-233°C; ir (Nujol) 3250 (s,$\equiv$C-H), 2070 (w,-C$\equiv$C-), 1720 and 1700 cm^{-1} (w,s,-O-CO-NH-).

Anal. Calcd for $C_{24}H_{24}N_2O_4$: C, 71.27; H, 5.98; N, 6.93
Found: C, 71.55; H, 5.76; N, 6.75

33. 5,5'-(Ethylene)bis(3-phenyl-4-methylene-5-methyl-2-oxazolidone) (53)

Procedure 1

A solution of 0.6260 g (0.005 mol) of phenyl isocyanate in 3 ml of anhydrous NMP was slowly added to a solution of 0.5367 g (0.0025 mol) of 3,6-dihydroxy-3,6-dimethyl-1,7-octadiyne and 0.014 g of sodium methoxide in 7 ml of NMP. The mixture was stirred at ambient temperature for 12 hr and then added to ice water. The white precipitate that formed was recrystallized from ethanol to afford a white powder: np 173-175°C; ir (KBr) 3230 (s,$\equiv$C-H), 2100 (w,-C$\equiv$C-) and 1750 cm^{-1} (s,oxazolidone).

Procedure 2

A solution of 1.8244 g (0.015 mol) of phenyl isocyanate in 10 ml of anhydrous DMF was slowly added to a solution of 1.2728 g (0.0077 mol) of 3,6-dihydroxy-3,6-dimethyl-1,7-octadiyne and 3 ml of triethylamine in 15 ml of DMF. The mixture was heated at reflux for 12 hr and then added to 250 ml of ice water to afford a 90% yield of a yellow-brown precipitate. The crude product was recrystallized from 90% ethanol to give a 76% yield of pure white powder: mp 250-251°C; ir (KBr) 3105 (w, =C $\genfrac{}{}{0pt}{}{H}{H}$), 1760 (s, oxazolidone C=O), 1670, 1635 and 815 cm^{-1} (m,m,w, C=CH$_2$); nmr (CDCl$_3$) δ 7.44 (m, 10H, C$_6$H$_5$), 4.18 (q, 4H,=CH$_2$), 2.03 (s, 4H, -CH$_2$CH$_2$-) and 1.64 ppm (s, 6H, -CH$_3$).

<u>Anal.</u> Calcd for C$_{24}$H$_{24}$N$_2$O$_4$: C, 71.27; H, 5.98; N, 6.93

Found: C, 71.23; H, 5.84; N, 6.74

34. Reaction of MDI with 3-methyl-1-pentyn-3-ol

Procedure 1

A solution of 2.55 g (0.010 mol) MDI in 10 ml of anhydrous NMP was slowly added to a solution of 2.0 g (0.02) 3-methyl-1-pentyn-3-ol in 20 ml of NMP. (The NMP had been distilled under high vacuum into a dropping funnel containing the diisocyanate and also into the round-bottom flask containing the alkynol.) The mixture was stirred at ambient temperature for 120 hr and then added to water. The infrared spectrum of the product contained absorptions characteristic of urea and isocyanate moieties.

Procedure 2

Procedure 1 was repeated with ether as the solvent. After the reaction mixture was stirred at ambient temperature for 24 hr, the ether was removed under reduced pressure to yield starting material.

Procedure 3

Procedure 1 was repeated with 7 drops of triethylamine being added to the initial alkynol solution. The yellow mixture was stirred at ambient temperature for 24 hr and then added to water to yield an insoluble gel.

Procedure 4

Procedure 1 was repeated with 0.05 g of DABCO being added to the initial alkynol solution. The mixture was stirred at ambient temperature for 24 hr and then added to water to give a quantitative yield of a white solid. The crude product was reprecipitated from methylene chloride with petroleum

ether to afford a white powder: mp 174-176°C (d); ir (KBr) 3400 (N-H), 3300 ($\equiv$C-H), 3040 (Ar-H), 2980, 2960 (R-H), 1710 (-O-CO-NH-), and 1590 cm^{-1} (-CO-NH-).

     <u>Anal.</u> Calcd for C$_{27}$H$_{30}$N$_2$O$_4$:   C, 72.62;   H, 6.77;   N, 6.28

                             Found: C, 71.51;   H, 5.19;   N, 8.54

Procedure 5

To a solution of 1.2965 g (0.013 mol) of 3-methyl-1-pentyn-3-ol and 1 drop of Nuocure 28 (0.01g) in 15 ml of anhydrous DMF was slowly added a solution of 1.6529 g (0.066 mol) of MDI in 10 ml of anhydrous DMF. After the addition, which was carried out under nitrogen, was complete, the mixture was stirred under nitrogen at ambient temperature for 20 hr. A portion of the reaction mixture was removed, added to crushed ice, and filtered. The infrared spectrum of the white solid obtained contained a weak absorption at 1640 cm^{-1} indicating possible urea contamination. Hence, the remainder of the reaction mixture was stirred an additional 48 hr under nitrogen at ambient temperature. The solution was added to crushed ice and filtered to afford a white solid. The infrared spectrum of the crude product still contained a weak band at 1640 cm^{-1}. The product was recrystallized from a benzene-heptane mixture to afford white crystals: mp 145.5-146°C; ir (KBr) 3250 (s,$\equiv$C-H) 2090 (w, -C$\equiv$C-) and 1700 cm^{-1} (s,-O-CO-NH-); nmr (Unisolve) δ 8.7 (s, 2H, -NH), 7.15 (q, 8H, C$_6$H$_4$), 3.7 (s, 2H, Ar-CH$_2$-Ar), 2.65 (s, 2H, $\equiv$C-H), 1.75 (q, 4H, -CH$_2$-), 1.67 (s, 6H, -CH$_3$), and 1.0 ppm (t, 6H, CH$_3$-).

     <u>Anal.</u> Calcd for C$_{27}$H$_{30}$N$_2$O$_4$:   C, 72.62;   H, 6.77;   N, 6.28

                             Found: C, 72.81;   H, 6.82;   N, 6.46

35.   <u>3,3'-(Methylenedi-p-phenylene)bis(4-methylene-5-ethyl-5-methyl-2-oxazolidone (56)</u>

Procedure 1

A solution of 0.6257 g (0.0025 mol) in 10 ml of DMF was slowly added to a solution of 0.4907 g (0.005 mol) 3-methyl-1-pentyn-3-ol and 3 ml of triethylamine in 15 ml of toluene. The mixture was heated at 80°C for 24 hr and then added to water to afford an off-white precipitate. The infrared spectrum of the crude product showed weak oxazolidone absorptions and strong urea absorptions.

Procedure 2

A solution of 1.5271 g (0.006 mol) of MDI in 10 ml of anhydrous DMF was slowly added to a refluxing solution of 1.1979 g (0.012 mol) 3-methyl-1-pentyn-3-ol, 1 ml of triethylamine and 15 ml of anhydrous DMF. The reaction

mixture was heated at reflux for an additional 15 hr and then added to 250 ml of ice water. The precipitate that formed was collected by filtration, dried, and reprecipitated from methylene chloride with petroleum ether to yield 2.2973 g (84%) of the off-white product: mp 128-128.5°C; ir (Nujol) 1760 (oxazolidone C=O) 1680, 1650, and 820 cm^{-1} (C=CH$_2$); nmr (CDCl$_3$) δ 7.36 (m, 8H, C$_6$H$_4$), 4.18 (q, 4H, = CH$_2$), 4.10 (s, 2H, -CH$_2$-), 1.65 (m, 10H, -CH$_2$, -CH$_3$), and 1.15 ppm (t, 6H, -CH$_3$).

Anal. Calcd for C$_{27}$H$_{30}$N$_2$O$_4$: C, 72.62; H, 6.77; N, 6.28

Found: C, 72.88; H, 6.94; N, 6.24

36. Reaction of HDI with 3-methyl-1-pentyn-3-ol

Procedure 1

HDI (2.74 g, 0.016 mol) was slowly added to a solution of 4.00 g (0.041 mol) 3-methyl-1-pentyn-3-ol in 15 ml of anhydrous DMF. The mixture was stirred at ambient temperature for 24 hr and then added to ether. Only unreacted starting material could be recovered from the ether solution.

Procedure 2

To a solution of 2.2070 g (0.0225 mol) of 3-methyl-1-pentyn-3-ol and 4 drops of Nuocure^R 28 (0.04 g) in 15 ml of anhydrous DMF was slowly added a solution of 1.8456 g (0.0110 mol) of HDI in 10 ml of anhydrous DMF. After the addition, which was carried out under nitrogen, was complete, the mixture was added to crushed ice and filtered to afford a quantitative yield of white solid. The product was recrystallized from petroleum ether to afford white crystals; mp 69.5-70.5°C; ir (KBr) 3250 (s, $\equiv$CH), 2120 (w, -C$\equiv$C-) and 1690 cm^{-1} (s, -O-CO-NH-).

Anal. Calcd for C$_{20}$H$_{32}$N$_2$O$_4$: C, 65.90; H, 8.85; N, 7.69

Found : C, 65.26; H, 8.81; N, 7.61

37. 3,3'-(Ethylene)bis(3-methyl-4-methylene-5-propyl-2-oxazolidone (60)

A solution of 0.4256 g (0.005 mol) of propyl isocyanate in 10 ml of anhydrous DMF was slowly added to a solution of 0.4153 g (0.0025 mol) of 1,3-dihydroxy-3,5-dimethyl-1,7-octadiyne and 1 ml of triethylamine in 15 ml of DMF. After the mixture was heated at reflux for 32 hr, the DMF was removed under reduced pressure. The oily residue was dissolved in acetone and the solution added to ice water to afford a 90% yield of a yellow-brown precipitate. The crude product was recrystallized from ethanol to give a 77% yield of a white powder: mp 127-129°C; ir (Nujol) 1750 (s, oxazolidone

c=O), 1675, 1635 and 825 cm^{-1} (m, n, w, C=CH$_2$).

    <u>Anal.</u> Calcd for C$_{18}$H$_{28}$N$_2$O$_4$:   C, 64.26; H, 8.39; N, 8.33

                                  Found :   C, 64.52; H, 8.63; N, 8.28

    38.   <u>Polymerization of TDI with 3,6-dihydroxy-3,6-dimethyl-1,7-octadiyne</u>

        <u>Procedure 1</u>

        Into a 50-ml, 3-neck, round-bottom flask was placed 1.0435 g (6.2781 mmol) of the bisalkynol dissolved in 10 ml of dry DMF. A solution of 1.0934 g (6.2781 mmol) of the diisocyanate in 5 ml of dry DMF was then added dropwise under a nitrogen atmosphere. The mixture was stirred for 3 days at ambient temperature. During this time the solution became very viscous and gradually gelled. The gel was diluted with DMF and poured into ether. The polymer that precipitated was triturated with hexane and dried at 110°C under vacuum for 24 hr. The product was completely insoluble in common organic solvents.

        <u>Procedure 2</u>

        To avoid side reactions with water, a special piece of glassware was prepared that allowed all the reagents to be maintained under high vacuum during their mixing and throughout the polymerization. NMP (10 ml) was distilled under vacuum into a reaction vessel containing 0.2631 g (1.511 mmol) of the bisalkynol. The diisocyanate [0.2511 g (1.511 mmol)] was then slowly distilled under vacuum into the reaction mixture. After the reaction was stirred at ambient temperature for 24 hr, it was slowly added to water. The polymer that precipitated was collected by filtration and dried under vacuum. The polymer's infrared spectrum contains absorptions characteristic of carbamate, urea, and acetylene groups. (η inh = 0.14, 0.250 g/dl in DMF at 30°C)

        <u>Procedure 3</u>

        Using Procedure 2, 1.2232 g (7.023 mmol) of the diisocyanate was polymerized with 1.1676 g (7.024 mmol) of the bisalkynol in 10 ml of NMP. The reaction was stirred at ambient temperature for 3 days. After this time, the solution showed no marked increase in viscosity. Hence, the reaction temperature was increased to 50°C for 24 hr and then to 100°C for 12 hr. The reaction was added to ether, and the polymer that precipitated collected by filtration. The polymer's IR spectrum contains absorptions characteristic of carbamate and oxazolidone structures. (η inh =0.10, 0.250 g/dl in DMF at 30°C)

Procedure 4

A solution of 1.9673 g (10.0 mmol) of TDI in 10 ml of DMF was slowly added to a refluxing solution of 1.8775 g (10.0 mmol) of the bisalkynol and 1 ml of triethyamine in 15 ml of DMF. The mixture was heated at reflux for 12 hr and then added to water to afford a brown precipitate. The crude product was reprecipitated from methylene chloride with petroleum ether to give a yellow powder. The infrared spectrum of the product showed absorptions characteristic of oxazolidone, urethane, and urea moieties. (η inh = 0.04, 0.27 g/dl in DMF at 30°C)

Procedure 5

A solution of 1.12276 g (6.45 mmol) of TDI in 10 ml of toluene was slowly added to a solution of 1.07151 g (6.45 mmol) of bisalkynol and 1 ml of triethylamine in 15 ml of toluene. After the mixture was heated at reflux for 4 hr, a white solid precipitated. The infrared spectrum of the product showed absorptions characteristic of urethane and oxazolidone moieties. (η inh = 0.03, 0.25 g/dl in DMF at 30°C)

39. Polymerization of MDI and 3,6-dihydroxy-3,6-dimethyl-1,7-octadiyne

Procedure 1

To a solution of 3.4189 g (20.57 mmol) of the bisalkynol and 0.13 g of DABCO in 20 ml of NMP was slowly added 5.1478 g (20.57 mmol) of the diisocyanate dissolved in 15 ml of NMP. The addition funnel was rinsed with 5 ml of NMP to insure complete addition of the diisocyanate. The polymer solution turned pale yellow immediately and became notably more viscous in 3 hr. After 25 hr at ambient temperature, the reaction mixture appeared to gel. The mixture was allowed to stand an additional 3 days, and then poured into 150 ml of ice water. The fibrous solid that precipitated was reprecipitated from acetone with pet. ether to afford the off-white product; ir (KBr) 3400 (-N-H), 3280 ($\equiv$C-H), 2100 (-C$\equiv$C-H), and 1700 cm^{-1} (-O-CO-NH); η_{inh} = 0.36 (0.250 g/dl in DMF at 30°C).

Procedure 2

To a solution of 1.16040 g (6.98 mmol) of 3,6-dimethyl-1,7-octadiyn-3,6-diol and 0.1 g of freshly sublimed DABCO in 10 ml of anhydrous DMF was slowly added a solution of 1.74713 g (6.98 mmol) of MDI in 10 ml of anhydrous DMF. After the addition, which was carried out under a positive pressure of nitrogen, was complete, the mixture was stirred under nitrogen at ambient temperature for 24 hr. During this time the reaction mixture gelled. The gel was added to water to afford a fibrous white solid. The product was insoluble in organic solvents.

Procedure 3

To a solution of 1.647174 g (0.88 mmol) of 3,6-dimethyl-1,7-octadiyn-3,6-diol and 4 drops of Nuocure[R] 28 (0.04 g) in 10 ml of anhydrous DMF was slowly added a solution of 2.47186 g (0.88 mmol) of MDI in 10 ml of anhydrous DMF. After the addition, which was carried out under a positive pressure of nitrogen, was complete, the mixture was stirred under nitrogen at ambient temperature for 80 hr. The reaction mixture was added to ice water to precipitate a white fibrous solid. The infrared spectrum of this polymer shows a band at 1640 cm^{-1} indicating that the polymerization reaction was not complete (η_{inh} = 0.38, 0.50 g/dl in DMF at 30°C).

Procedure 4

To a solution of 0.75552 g (4.55 mmol) of 3,6-dimethyl-1,7-octadiyn-3,6-diol and 3 drops of Nuocure[R] 28 (0.03 g) in 10 ml of anhydrous DMF was slowly added a solution of 1.13754 g (4.55 mmol) of MDI in 10 ml of anhydrous DMF. After the addition, which was carried out under a positive pressure of nitrogen, was complete, the mixture was stirred under nitrogen at room temperature (15-20°C) for 6 days. A small portion (1 ml) of the product that precipitated contained absorption bands at 2250 (-NCO), 1710 (-O-CO-NH-), and 1640 cm^{-1} (-NH-CO-NH-). The reaction mixture was then heated at 30°C for 1 day. A small portion was removed and added to ice water. The infrared spectrum of the product that precipitated showed a more intense urethane absorption, a decreased urea absorption, and no isocyanate absorptions. The mixture was then heated at 40°C for 1 day. A small protion was again removed and added to ice water. The infrared spectrum of the product that precipitated showed a considerable decrease in the urea absorption at 1640 cm^{-1}. After the mixture was heated at 40°C for an additional day, another small portion was removed and added to ice water. The infrared spectrum of the product that precipitated showed only a slight decrease in the band at 1640 cm^{-1}. The mixture was then heated at 40°C for 2 days. The infrared spectrum of a small sample of the product obtained as described above was identical to the spectrum of the sample taken 2 days earlier. The reaction mixture was divided into two equal halves. One half was slowly added to water to precipitate a white, fibrous polymer. (η_{inh} = 0.23, 0.5 g/dl in DMF at 30°C) In order to end-cap any unreacted isocyanate groups, 0.5 ml of 3-methyl-1-pentyn-3-ol was added to the remaining half and the resulting mixture stirred at 40°C for 8 hr. This mixture was then

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poured into water. The IR spectrum of the polymer that precipitated was identical to that of the polymer obtained from the untreated half of the original reaction mixture. This indicates that the small urea contamination present in both samples must result from fortuitous water present during the polymerization rather than from the water used in the work-up.

Procedure 5

To a solution of 0.02103 g (5.54 mmol) of 3.6-dimethyl-1,7-octadiyn-3,6-diol and 3 drops of Nuocure^R 28 (0.03 g) in 10 ml of anhydrous DMF was slowly added a solution of 1.38537 g (5.54 mmol) of MDI in 20 ml of anhydrous DMF. After the addition, which was carried out under a positive pressure of nitrogen, was complete, the mixture was stirred under nitrogen at 40°C for 1 day. The reaction mixture was then concentrated to 10 ml total volume by removing DMF under reduced pressure. After the reaction was allowed to proceed an additional 3 days at 40°C, the mixture was added to ice water. The white, fibrous solid that precipitated was dried under reduced pressure. The IR spectrum of the product indicated a small amount of urea contamination. The polymer was extracted with benzene overnight and then dried under reduced pressure. The infrared spectrum of the purified sample shows no urea absorptions, but it contains strong absorption bands at 3250 ($\equiv$C-H), 2100 (-C$\equiv$C-), and 1700 cm^{-1} (-O-CO-NH-). (η_{inh} = 0.54, 0.5 g/dl in DMF at 30°C).

Procedure 6

Procedure 5 was repeated with MEK as the solvent. After the mixture was stirred at 40°C for 36 hr, a white solid begun to precipitate. The mixture was stirred an additional 12 hr at 40°C and then added to petroleum ether. The white, fibrous product was extracted with benzene overnight. The infrared spectrum of the polymer is identical to that of the polymer obtained by Procedure 5. (η_{inh} = 0.31, 0.5 g/dl in DMF at 30°C)

Procedure 7

Procedure 5 was repeated with sulfolane as the solvent. After the mixture was stirred at 40°C for 36 hr, a white solid began to precipitate. After the mixture was stirred an additional 24 hr at 40°C, it was diluted with DMF and then added to water. The white, fibrous product was extracted with benzene overnight. The infrared spectrum of the polymer is identical to that of the polymer obtained by Procedure 5. (η_{inh} = 0.27, 0.5 g/dl in DMF at 30°C)

Procedure 8

A solution of 2.5025 g (0.01 mol) MDI in 10 ml of DMF was slowly added to a refluxing solution of 1.6621 g (0.01 mol) of bisalkynol and 1 ml of triethylamine in 15 ml of DMF. The mixture was heated at reflux for 16 hr and then added to water to afford 4.15 g (99%) of a white polyoxazolidone: η_{inh} = 0.37 (0.250 g/dl in DMF at 30°C); ir (Nujol) 1760 (s, oxazolidone C=O), 1680, 1650, and 820 cm^{-1} (m, m, m, C=CH$_2$).

40. Polymerization of HDI and 3,6-dihydroxy-3,6-dimethyl-1,7-octadiyne

Procedure 1

To a solution of 0.8318 g (5.00 mmol) of 3,6-dimethyl-1,7-octadiyn-3,6-diol and 3 drops of Nuocure^R 28 (0.03 g) in 10 ml of anhydrous DMF was slowly added a solution of 0.8418 g (5.00 mmol) of HDI in 10 ml of anhydrous DMF. After the addition, which was carried out under nitrogen, was complete, the mixture was stirred under nitrogen at 35-40°C for 40 hr. A small portion (1 ml) of the mixture was removed and added to water. The infrared spectrum of the product that precipitated contained an isocyanate absorption at 2250 cm^{-1} indicating that the reaction was not complete. Hence, the mixture was stirred an additional 25 hr at 35-40°C. A small portion of the mixture was removed and added to water. The infrared spectrum of the white, fibrous product that precipitated contained a urethane absorption at 1710 cm^{-1} and no absorptions characteristic of isocyanate or urea groups. Approximately one-half of the mixture was then added to water to afford a white polymer with an inherent viscosity of 0.25 (0.50 g/dl in DMF at 25°C). The remaining one-half of the mixture was stirred an additional 3 days at 40°C and then added to water. The inherent viscosity of the solid that precipitated was also 0.25.

Procedure 2

Procedure 1 was repeated with sulfolane as the solvent. After the reaction mixture was stirred 24 hr at 40°C, a white solid began to precipitate. DMF (15 ml) was then distilled into the reaction flask, and the resulting solution, which cleared upon the addition of DMF, was stirred an additional 2 days at 40°C. The mixture was added to ice water to afford a white, fibrous mat. The product was reprecipitated from DMF with water to give a white, fibrous material: η_{inh} = 0.41 (0.5 g/dl in DMF at 30°C); ir (KBr) 3330 (m, NH), 3250 (m, ≡C-H), 2100 (w, -C≡C-), and 1710 cm^{-1} (s, -O-CO-NH-).

Procedure 3

A solution of 3.19491 g (0.02 mol) of HDI in 10 ml of DMF was slowly added to a refluxing solution of 3.15711 g (0.02 mol) bisalkynol and 1 ml of

triethylamine in 15 ml of DMF. The mixture was stirred at reflux for 32 hr and then added to water to afford a brown precipitate: η_{inh} = 0.07 (0.5 g/dl in DMF at 30°C); ir (Nujol) 1760 (s, oxazolidone C=O), 1675, 1635, and 815 cm^{-1} (m,m,m, C=CH$_2$).

41. **Intramolecular cyclization of model compound 55**

Procedure 1

A solution of 0.250 g biscarbamate 55 and 0.001 g sodium methoxide in 2 ml NMP was stirred at ambient temperature for 24 hr. The reaction mixture was added to 50 ml of cold water containing 1 drop of conc. H$_2$SO$_4$ to precipitate an off-white solid. The product was dried, dissolved in methylene chloride, and reprecipitated in petroleum ether: ir (KBr) 3400 (m, NH), 3300 (m, ≡C-H), 2100 (w, -C≡C-), 1760 (s, oxazolidone C=O), and 1710 cm^{-1} (s, -O-CO-NH).

Procedure 2

Procedure 1 was repeated with the reaction mixture being stirred at 75°C for 2 hr and then at ambient temperature for 24 hr. The infrared spectrum of the product was nearly identical to that of the product obtained in Procedure 1.

Procedure 3

Procedure 1 was repeated with the reaction mixture being stirred at 60°C for 24 hr. Precipitation in water afforded a quantitative yield of the bisoxazolidone 56.

Procedure 4

A solution of 2.0 g of 55 in 15 ml of DMF was treated with two drops of a 50% solution of benzyltrimethylammonium hydroxide in methanol (Triton B). The mixture, which immediately turned light yellow, was stirred for 15 min at ambient temperature and then added to water to afford a quantitative yield of bisoxazolidone 56.

42. **Intramolecular cyclization of polyurethane 62**

A solution of 0.5834 g of polymer 62 (η_{inh} = 0.4, 0.5 g/dl in DMF at 30°C) was treated with 3 drops of Triton B. The mixture, which immediately turned light yellow, was stirred at ambient temperature for 15 min and then added to water to afford a quantitative yield of polyoxazolidone 63 (η_{inh} = 0.16 , 0.5 g/dl in DMF at 30°C).

C. Transparent, Thermally-Stable Polymers

   1. Carboxylated polyphenylenes 66 and 68

   Polymers 66 and 68 were prepared by the polymerization of 3,3'-(oxydi-p-phenylene)bis[2,4,5-triphenylcyclopentadienone] and 3,3'-(oxydi-p-phenylene)bis[2,5-diethoxycarbonyl-4-phenylcyclopentadienone] with p-diethynyl-benzene and 4,4'-diethynyldiphenyl ether by the known procedure.[4]

   2. Aromatic ionomers 67 and 69

   The ionomers were prepared by the hydrolyses of 66 and 68 in refluxing ethylene glycol containing potassium hydroxide according to the known procedure.[4]

   3. Hydrolysis of polymer 66 in 1,4-butanediol

   To a solution of 40.0 g of potassium hydroxide in 200 ml of dry 1,4-butanediol was added 6 g of polymer 66. The resulting heterogeneous mixture was heated at reflux for 48 hr and then added to water. The off-white polymer that precipitated was collected by filtration, washed with 2 ℓ of water, and air dried.

   4. Hot pressing of polymer 66

   The hot pressing of polymer 66 was carried out in the following manner. A 0.100 g sample of the ionomer was placed in a preheated Beckman number 5020 KBr die and the apparatus then reheated to the desired temperature for 10 min. The die was removed from the oven and pressed between heated metal platens at the desired temperature (250°C max.) and at a gauge pressure of 22,000 lbs using a Model C Carver Laboratory press. The pressure was was maintained for 5 min and the die then removed and cooled. The pellet was removed and its height measured with a micrometer. The volume of each pellet was determined using the formula for the volume of a cylinder $V = \pi r^2 h$.

   5. Barium ionomer 71

   A 0.5 g sample of ionomer 66 was stirred in 50 ml of refluxing concentrated hydrochloric acid for 18 hr. The resulting polymer was continuously extracted with water for 24 hr, dried for 4 hr at 150°C under vacuum, and then added to a hot solution of 6.0 g of barium acetate in 50 ml of ethylene glycol. The heterogeneous mixture was heated at reflux for 18 hr. The barium ionomer was collected by filtration, continuously extracted with water for 24 hr, and then dried under vacuum at 150°C for 12 hr.

6. Reduction of 4-(2,4-dinitrophenoxy)phenylacetylene (72)

Procedure 1

To a rapidly stirred solution of 41 g (230 mmol) of sodium hydrosulfite and 32 g (230 mmol) of potassium carbonate in 250 ml of water was slowly added a solution of 6.7 g (23.4 mmol) of compound 72 in 50 ml of dioxane. The reaction mixture became hot as the solution changed from yellow to white. After the mixture was stirred for 30 min the dioxane was removed under reduced pressure. The aqueous solution was repeatedly extracted with methylene chloride. The solvent was removed under reduced pressure to afford 0.2 g of brown oil that could not be further purified: ir (neat)3450, 3350 (N-H), 3280 and 2100 cm^{-1} (C≡C-H).

The following modifications of the above procedure were carried out in attempts to increase the yield:

1. Methanol, THF, DMF, DMAC, and ethanol were used in place of dioxane.
2. No organic solvent was used.
3. Ammonium hydroxide and sodium hydroxide were used in place of potassium carbonate.[40]
4. Solid sodium hydrosulfite was added in portions to a mixture of the dinitro compound, base, water, and the organic solvent.[40]
5. A molar ratio of compound 72 to base of 1:15 was used.
6. The reaction was carried out under nitrogen.
7. After removal of the organic solvent, the aqueous solution was made strongly acidic with hydrochloric acid and concentrated to 50 ml.
8. Extraction was carried out with ethyl acetate.

In all modifications, the reaction mixture became hot indicating reduction was taking place. However, only very small amounts of crude product could be isolated.

Procedure 2[41]

To a mixture of 160 g (1.052 mol) ferrous sulfate, 35 ml ethanol, 8.0 g (0.028 mol) compound 72, and 260 ml of water, which had been heated at reflux under nitrogen for 2 hr, was slowly added 55 ml of concentrated ammonium hydroxide. The reaction mixture was heated at reflux overnight, an additional 30 ml of ammonium hydroxide was added, and the mixture allowed to cool for one hr. The solution was filtered, and the precipitated iron hydroxides washed with ether. After the filtrate was extracted several times with ether, the extracts were combined and dried over anh potassium carbonate. However, no product was isolated when the ether was removed under reduced pressure.

A mixture of 7.2 g (0.025 mol) compound 72, 120 g (1.83 mol) of zinc dust, 4 g calcium chloride in 6 ml of water, and 200 ml of 78% ethanol was heated at reflux for 8 hr under nitrogen. The hot solution was filtered, and the sludge of zinc dust was washed with hot ethanol. The filtrate was reduced to low volume under reduced pressure, acidified with 10% hydrochloric acid, washed with ether, neutralized with 10% sodium hydroxide, and extracted several times with ether. The combined ether extracts were washed with a saturated solution of sodium chloride and dried over anh sodium sulfate. The ether was removed under reduced pressure to afford 3.2 g of a dark brown oil. The infrared indicated that the nitro groups had been reduced, however, the spectrum did not show any acetylenic absorptions: ir (neat) 3450 and 3350 cm^{-1} (N-H).

Procedure 5 [43]

A mixture of 1 g (3 mmol) of compound 72, 35 ml of ethyl acetate, 1.7 g (28 mmol) of Raney nickel (W2), 7 ml of water, and 35 ml of ethanol was shaken under 15 psi of hydrogen at room temperature for 2 hr. The reaction mixture was reduced to low volume under reduced pressure. The filtrate was acidified with 10% hydrochloric acid, washed with ether, neutralized with 20% sodium hydroxide, and extracted several times with ether. The ether was removed under reduced pressure to afford a brown oil which did not show acetylenic infrared absorptions: ir (neat) 3450 and 3350 cm^{-1} (N-H).

Procedure 6 [30]

A mixture of 8.5 g (0.03 mol) of 72, 15.0 g (0.23 g atom) of zinc, 75 ml of THF, 40 ml of concentrated ammonium hydroxide, and 30 ml of water was stirred for 24 hr under nitrogen. The resulting reaction mixture was repeatedly extracted with 150 ml portions benzene. The combined benzene extracts were washed once with 50 ml of water, dried over anh sodium sulfate, and concentrated to about 3 ml. Dropwise addition of this benzene solution to about 10 ml of hexane followed by cooling in a dry ice-acetone bath resulted in pale yellow crystals. Sublimation of this crude diamine at 120°C under high vacuum (>1 mm) yielded 0.4 g (8%) of a colorless compound: mp 109-110°C, ir (KBr) 3450, 3350 cm^{-1},(m,m,NH$_2$), 3300 and 2100 cm^{-1} (≡CH); nmr(CDCl$_3$) 3.05δ (s, 1H, CH), 3.65 (s, 4H, NH$_2$), 7.3 (s, 4H, p-C$_6$H$_4$) and 6.8 (m, 3H, 1,2,4-trisubstituted aromatic ring).

Anal. Calcd for C$_{14}$H$_{12}$N$_2$O: C, 74.97; H, 5.4; N, 12.49.
Found: C, 74.86; H, 5.5; N, 12.47.

7. Attempted preparation of [4-(2,4-dinitrophenoxy)phenylethynyl]-
   trimethylsilane (74)

   Treatment of 4-(2,4-dinitrophenoxy)phenylacetylene with butyl

lithium followed by trimethylchlorosilane as described [32] gave a black tar that

could not be further purified.

8. 2,4-Diacetamidophenol (77)

   The compound was prepared from 2,4-diaminophenol dihydrochloride by

the known procedure [44]: mp 222-224°C (lit [44] 225°C).

9. (4-Fluoro-1-chloropropen-3-al)benzene

   The reaction of a DMF/POCl$_3$ complex with 4-fluoroacetophenone

according to the described procedure [54] resulted in a 44% yield of product:

mp 69-70°C ir (KBr) 2880 cm^{-1} (C-H formyl) 1680 cm^{-1} (s,C=O).

10. Attempted preparation of 4-fluorophenylacetylene (79b)

    Treatment of (4-fluoro-1-chloropropen-3-al)benzene with sodium

hydroxide under the conditions described [54] yielded an oil which could not

be further purified.

11. 4-Fluorophenylacetylene (79b)

    The compound was prepared from 4-fluoroacetophenone by the known

procedure [45] bp 60-65°C (200 mm) (lit. [45] 34-35°C (10 mm).

12. Sodium 2,4-diacetamidophenolate (78)

    Treatment of 2,4-diacetamidophenol with sodium methoxide under

the conditions described [4] resulted in a quantitative yield of the product.

13. Attempted preparation of 4-(2,4-diacetamidophenoxy)phenylacetylene (80)

    Procedure 1

    Treatment of sodium 2,4-diacetamidophenolate with 4-bromophenylacetylene

under the conditions described [4] yielded an unidentifiable black tarry product.

    Procedure 2

    Reaction of 2,4-diacetamidophenol with 4-flurophenylacetylene according

to the described procedure [46] resulted in an unidentifiable black tar.

14. 4-(2,4-Dinitrophenoxy)acetophenone (81)

    A mixture of 13.6 g (0.1 mol) of 4-hydroxyacetophenone, 5.4 g (0.1

mol) of sodium methoxide and 50 ml of benzene was heated at reflux for 1 hr.

After the removal of benzene by distillation, 50 ml of toluene and 20.2 g

(0.1 mol) of 2,4-dinitrochlorobenzene was added. The mixture was then

heated at reflux for 15 hr and filtered. The crude product, which

precipitated from the filtrate upon cooling, was recrystallized from ethanol

to yield 13.5 g (45%) of the pale yellow crystals: mp 134-135°C (lit [47]

134.5-135.5°C), ir (KBr) 1660 cm^{-1} (s, C=O), 1570 and 1330 cm^{-1} (s, NO$_2$).

15. <u>4-(2,4-Diaminophenoxy)acetophenone (82)</u>

A mixture of 11.0 g (0.036 mol) of 4-(2,4-dinitrophenoxy)acetophenone, 13.6 g (0.11 g atom) of tin and 280 ml of 10% hydrochloric acid was heated on a boiling water bath for 2 hr.[48] After the reaction was allowed to cool, it was stirred with 1.0 g of decolorizing carbon and filtered. The filtrate was deoxygenated by bubbling nitrogen and then treated with deoxygenated 40% sodium hydroxide, under nitrogen. The crude product was repeatedly washed with deoxygenated cold water, till the washings were neutral to litmus. Recrystallization from ethanol gave 5.0 g (57%) of colorless crystals: mp 104-106°C, ir (KBr) 3460 and 3360 cm^{-1} (m, NH$_2$), 1650 cm^{-1} (s, C=O).

<u>Anal.</u>Calcd for C$_{14}$H$_{14}$N$_2$O$_2$: C, 69.40; H, 5.82; N, 11.56.

Found: C, 68.78; H, 5.79; N, 11.86.

16. <u>4-(2,4-Diacetamidophenoxy)acetophenone (83)</u>

A mixture of 4.4 g (0.018 mol) of 4-(2,4-diaminophenoxy)acetophenone, 36.0 g (0.35 mol) of acetic anhydrice, 34.1 g (0.57 mol) of glacial acetic acid and 0.10 g zinc dust was heated at reflux for 30 min. The reaction mixture was poured into 70 ml of cold water and filtered. The crude product was recrystallized from ethanol to yield 4.5 g (76%) of colorless crystals: mp 183-185°C; ir (KBr) 3350 cm^{-1} (s,NH), 1680 cm^{-1} (s, C=O).

<u>Anal.</u> Calcd for C$_{18}$H$_{18}$N$_2$O$_4$: C, 66.24; H, 5.56; N, 8.59.

Found: C, 66.05; H, 5.34; N, 8.74.

17. <u>Attempted preparation of 4-(2,4-diacetamidophenoxy)-1-chloropropen-3-albenzene</u>

The reaction of a DMF/POCl$_3$ complex with 4-(2,4-diacetamidophenoxy)-acetophenone according to the described procedure [54] resulted in an oily product that could not be identified.

18. <u>Attempted preparation of 4-(2,4-diacetamidophenoxy)-1,1-dichloro-ethylbenzene</u>

Treatment of 4-(2,4-diacetamidophenoxy)acetophenone with phosphorous pentachloride according to the described procedure [49] resulted in an unidentifiable black tarry product.

19. <u>(4-Bromophenylethynyl)trimethylsilane (87)</u>

The compound was prepared from 4-bromoacetophenone by the known procedure [34]: mp 60-62°C (lit [34] 62°C).

20. <u>3,5-Dinitrobenzoyl chloride</u>

The compound was prepared from 3,5-dinitrobenzoic acid by the known procedure [50]: mp 67-68°C (lit [50] 69.5°C).

21. Attempted preparation of (4-(3,5-dinitrobenzoyl)phenylethynyl)-
trimethylsilane (90)

Procedure 1

Acylation of phenylethynyltrimethylsilane with 3,5-dinitrobenzoyl chloride in carbon disulfide using aluminum chloride as the catalyst as described [51] gave an unidentifiable black oil.

Procedure 2

Anhydrous cadmium chloride 7.3 g(0.04 mol) was added to a cold solution of 4-(phenylethynyltrimethylsilane)magnesium bromide (prepared in situ from 0.08 mol of 4-bromophenylethynyltrimethylsilane and 0.08 g atom of magnesium as described)[35] in 110 ml of THF. The reaction mixture was heated at reflux for 45 min under nitrogen, cooled to room temperature and treated with 15.0 g (0.065 mol) of 3,5-dinitrobenzoyl chloride in 50 ml of THF. After the resulting mixture was heated at reflux for 1 hr, it was cooled in an ice bath and 600 ml of cold water followed by 350 ml of 20% sulfuric acid was slowly added. The aqueous reaction mixture was extracted 3 times with 100-ml portions of benzene. The combined benzene extracts were washed successively with 50 ml of water, 50 ml of 5% sodium bicarbonate, 50 ml of water and finally with 50 ml of saturated salt solution. After drying over anhydrous sodium sulfate,most of the benzene was removed under reduced pressure and the residue was chromatographed on a dry column of silica gel to yield an unidentifiable dark brown compound.

22. 3,5-Diaminoiodobenzene dihydrochloride (93) [48]

To a suspension of 15.5 g (0.05 mol) of 3,5-dinitroiodobenzene in 250 ml of water, was added 34.7 g of granulated tin and 93 ml of concentrated hydrochloric acid. The mixture was heated on a steam bath for 1.5 hr with rapid stirring. During this time the dinitro compound dissolved giving a clear colorless solution. Hydrogen sulfide gas was then bubbled through the solution to precipitate tin as the sulfide. The precipitate was filtered and washed with hot water. The filtrate was concentrated under reduced pressure and allowed to cool to give 13.1 g (80.3%) of white crystals.

23. 3,5-Diacetamidoiodobenzene (94) [52]

To a stirred solution of 40 g (0.13 mol) of compound 88 in 250 ml of water was added 84 ml of acetic anhydride and a solution of 62 g of sodium acetate in 170 ml of water. The precipitate that formed was filtered, washed with cold water and air dried. Recrystallization from ethanol

yielded 25 g of the white product; mp 284-285°C; ir (KBr) 3330 cm^{-1} (-NH), 1680 cm^{-1} (-C=O).

24. <u>3,5-Diacetamidodiphenylacetylene (95)</u>

A mixture of 5 g (0.016 mol) of compound <u>89</u> and 2.6 g (0.016 mol) of cuprous phenylacetylide in 120 ml of HMPA was heated at 190° under nitrogen for 45 min. The reaction mixture was cooled, filtered, and added to 1 ℓ of ice water. The precipitate that formed was collected by filtration, washed several times with water, dried and stirred in hot absolute ethanol. The ethanol solution was filtered to remove cuprous iodide. The filtrate was reduced to low volume and allowed to cool to give 2.5 g (54.4%) of white product; mp 195-196°C; ir (KBr) 3280 cm^{-1} (-NH-) and 2220 cm^{-1} (-C≡C-).

<u>Anal.</u> Calcd for C$_{18}$H$_{16}$N$_2$O$_2$: C, 73.95: H, 5.52: N, 9.58.
Found: C, 73.84: H, 5.40: N, 9.53.

25. <u>3,5-Diaminodiphenylacetylene (96)</u>

To a solution of 90 g of potassium hydroxide in 80 ml of water and 250 ml of absolute ethanol was added 2 g (0.0096 mol) of 3,5-diacetamidodiphenylacetylene. The suspension was heated at reflux under nitrogen for 8 hr. The resulting clear solution was cooled and extracted with 2 50-ml portions of chloroform. The combined extracts were washed with water, dried over anhydrous potassium carbonate, reduced to low volume, and added to hexane. The precipitate that formed was dried and then recrystallized from benzene to yield 1.1 g (77%) of white crystals; mp 112-113°C; ir (KBr) 3360 cm^{-1} (-NH$_2$) (no acetylenic absorptions present); nmr 5.7-7.3 ppm (-Ar), 3.35 ppm (-NH$_2$).

<u>Anal.</u> Calcd for C$_{14}$H$_{12}$N$_2$: C, 80.73: H, 5.81: N, 13.45.
Found: C, 81.00: H, 5.86: N, 13.64.

26. <u>3,5-Bis(3,4,5,6-tetraphenylphthalimido)diphenylacetylene (98)</u>

In a dry 50 ml flask, equipped with a magnetic stirring bar, a nitrogen inlet, a condenser and a stopper were placed 0.1780 g (0.855 mmol) of 3,5-diaminodiphenylacetylene, 6 ml of <u>m</u>-cresol, and 0.078 g of isoquinoline. After the diamine had dissolved, 0.7734 g (7.73 mmol) of 3,4,5,6-tetraphenylphthalic anhydride was added in several portions over a period of 1 hr. The final portion of the dianhydride was added as a suspension in 2 ml of <u>m</u>-cresol. The mixture was then heated at reflux for 3 hr to yield a clear bright yellow solution. The condenser was then replaced by a short path distillation apparatus, and the <u>m</u>-cresol was removed by distillation. When the volume of the solution was approximately reduced to 4 ml the distillation was stopped, and the solution was allowed to cool. The solution was diluted with 5 ml of chloroform and added to 500 ml of absolute ethanol to yield

0.87 g (92%) of an off-white solid; mp 400-402°C; ir (KBr) 3010 cm^{-1} (Ar, -CH), 1715 and 1770 cm^{-1} (imide-C=O)

Anal. Calcd for: $C_{78}H_{48}N_2O_4$: C, 86.97: ~H, 4.49: N, 2.60.

Found: C, 86.98: H, 4.37: N, 2.42.

27. 3,5-Bis(tetraphenylphthalimido)-1,2-diphenylethane (99)

Compound (93) 0.3179 g (0.295 mmol) was dissolved in 100 ml of a 50:50 ethylacetate ethanol mixture, and treated with hydrogen (60 psi) in the presence of a Raney Nickel catalyst. When the uptake of hydrogen ceased, the hydrogenation was stopped. The mixture was filtered, and the filtrate evaporated to dryness to yield 0.27 g (85%) of crude product. The product was dissolved in a minimum amount of chloroform, and chromatographed on silica gel with a 50:50 chloroform:petroleum ether mixture. The second fraction collected was evaporated to dryness to give 0.19 g (60%) of the white product: mp 295-297°C; ir (KBr) 1720 and 1780 cm^{-1} (imide); nmr 6.6-7.2 ppm(m,-Ar), 2.0 ppm (s,-CH$_2$).

Anal. Calcd for: $C_{78}H_{52}N_2O_4$: C, 86.64 H, 4.85 N, 2.59.

Found: C, 86.40 H, 4.64 N, 2.69

28. Polymerization of 4-(2,4-diaminophenoxy)phenylacetylene (73) with the phenylated dianhydride (100)

Procedure 1

Polymerizing 4-(2,4-diaminophenoxy)phenylacetylene with the phenylated dianhydrice 100 as described[4] resulted in a crosslinked, insoluble polymer.

Procedure 2

In a dry, 25 ml, 3-necked flask equipped with a magnetic stirring bar, a nitrogen inlet, a short-path distillation apparatus and a stopper was placed 0.1120 g (0.544 mmol) of 4-(2,4-diaminophenoxy)phenylacetylene, 3 ml of m-cresol, and 0.05 g of isoquinoline. After the diamine had dissolved, 0.500 g (0.544 mmol) of the phenylated dianhydride 100 was added in several portions over a period of 1 hr. The final portion of the dianhydride was added as a suspension in 1 ml of m-cresol. The mixture was then stirred for 1 hr at room temperature to yield a viscous, bright-yellow polyamic acid solution. The stopper was replaced by an addition funnel, 3 ml of benzene was added and the temperature of the flask was increased until distillation commenced. The volume of the solution was maintained at approximately 5 ml by continually replacing the distillate with benzene. The distillation-addition cycle was carried out for 3 hr. After the viscous solution was allowed to cool, it was diluted with 15 ml of chloroform and slowly added to 400 ml

of vigorously stirred absolute ethanol, collected, and dried under vacuum
at 153°C for 24 hr to afford a 95% yield of product. Approximately one-half
of the polymer was placed in a 25 ml round-bottom flask and gradually
heated to 250°C for 3 hr. The heat treated polymer was stirred with 100 ml
of chloroform for 24 hr and filtered. The insoluble, crosslinked polymer
was dried under vacuum at 153°C for 24 hr.

29. Phenylethynyl-substituted phenylated polyimide (102)

The polymerization of 0.1825 g (0.876 mmo) 3,5-diaminodiphenyl-
acetylene and 0.8053 g (0.876 mmol) of 4,4'-(oxidi-1,4-phenylene)bis(3,5,6-
triphenylphthalic anhydride) was carried out under the same conditions
described above. The polymer was precipitated in 500 ml of absolute
ethanol, reprecipitated from chloroform with ethanol, and dried under
vacuum at 150°C to afford a 90% yield of the product. The polymer was then
heat treated at 350°C for 4 hr : η_{inh} = 0.67 (0.25 g/dl in sym-tetrachloro-
ethane at 30°C); ir (KBr) 3015 cm^{-1} (Ar-CH), 1720 and 1770 cm^{-1} (s,imide-C=O).

<u>Anal.</u> Calcd for: $C_{78}H_{46}N_2O_5$: C, 85.85: H, 4.25: N, 2.57.
Found: C, 85.16: H, 4.10: N, 2.38.

30. Copolymer from 4,4-diaminodiphenyl ether (A)

The copoymerization of 0.0136 g (0.065 mmol) of 3,5-diamino-
diphenylacetylene, 0.1181 (0.590 mmol) of 4,4'-diaminodiphenyl ether, and
0.6022 g (0.655 mmol) of 4,4'-(oxidi-1,4-phenylene)bis(3,5,6-triphenyl-
phthalic anhydride) was carried out by the procedure described for the homo-
polymer. The polymer was precipitated in 500 ml of absolute ethanol, and
dried in vacuum at 150°C to afford a 91% yield of the product: η_{inh} = 0.82
(0.251 g/dl in sym-tetrachloroethane at 30°C); ir (KBr) 3000 cm^{-1} (Ar,-CH),
1740 and 1780 cm^{-1} (s, imide C=O).

31. Copolymer from 4,4-diaminodiphenyl ether (B)

The copolymerization of 0.0458 g (mmol) of 3,5-diaminodipheny-
lacetylene, 0.1029 g (0.514 mmol) of 4,4'-diaminodiphenyl ether and 0.6744 g
(0.734 mmol) of 4,4'-(oxidi-1,4-phenylene)bis(3,5,6-triphenylphthalic
anhydride) was carried out as described for the previous copolymer to afford
a 90% yield of the product. η_{inh} = 0.69 (0.262 g/dl) in sym-tetrachloroethane
at 30°C); ir (KBr) 3000 cm^{-1} (Ar,-CH), 1730 and 1780 cm^{-1} (s,imide-C=O).

32. Copolymer from 3,3',4,4'-benzophenonetetracarboxylic dianhydride

The copolymerization of 0.077 g (0.374 mmol) of 3,5-diaminodiphenyl-
acetylene, 0.2996 g (1.496 mmol) of 4,4'-diaminodiphenyl ether and 0.6026 g

(1.87 mmol) of 3,3',4,4'-benzophenonetetracarboxylic dianhydride was carried out by the procedure described for the homopolymer. After the final portion of the dianhydride was added as a suspension in $\underline{m}$-cresol, the mixture was heated at reflux. However, the mixture almost immediately gelled. The polymeric gel was insoluble in organic solvents.

33. <u>3-Aminophenylacetylene (104)</u>

Nitration of acetophenone according to the known procedure[53] afforded a 37% yield of 3-nitroacetophenone. Treatment of this compound with phosphorous oxychloride/DMF provided a 30% yield of 3-nitro-β-chloro-cinnamaldehyde,[54] which upon addition of base was converted to 3-nitro-phenylacetylene in 50% yield. Reduction with ferrous sulfate/ammonia provided 3-aminophenylacetylene in 64% yield; n_D^{25} 1.6115 (lit[54] n_D^{22} 1.6172).

34. <u>N-3-Ethynylphenyl-3,4,5,6-tetraphenyphthalimide (105)</u>

The reaction of 1.0 g (8.536 mmol) of 3-aminophenylacetylene and 3.86 g (8.536 mmol) of tetraphenylphthalic anhydride was carried out under conditions similar to that described for model compound <u>98</u>. The syrupy liquid obtained was poured into 600 ml of petroleum ether. The precipitate that formed was collected by filtration, dissolved in 250 ml of benzene, and decolorized with charcoal. After the solution was filtered, the filtrate was reduced to low volume and added to petroleum ether. The solid that formed was collected by filtration, dried, and chromatographed on silica gel with chloroform. The first fraction collected was evaporated to dryness to yield 1.5 g (32%) of an off-white product; mp 273-275°C; ir (KBr) 3290 cm^{-1} (-C-H), 1710 and 1780 cm^{-1} (imide-C=O).

<u>Anal.</u> Calcd for $C_{40}H_{25}NO_2$: C, 87.09: H, 4.57: N, 2.54.

Found: C, 87.37: H, 4.63: N, 2.40.
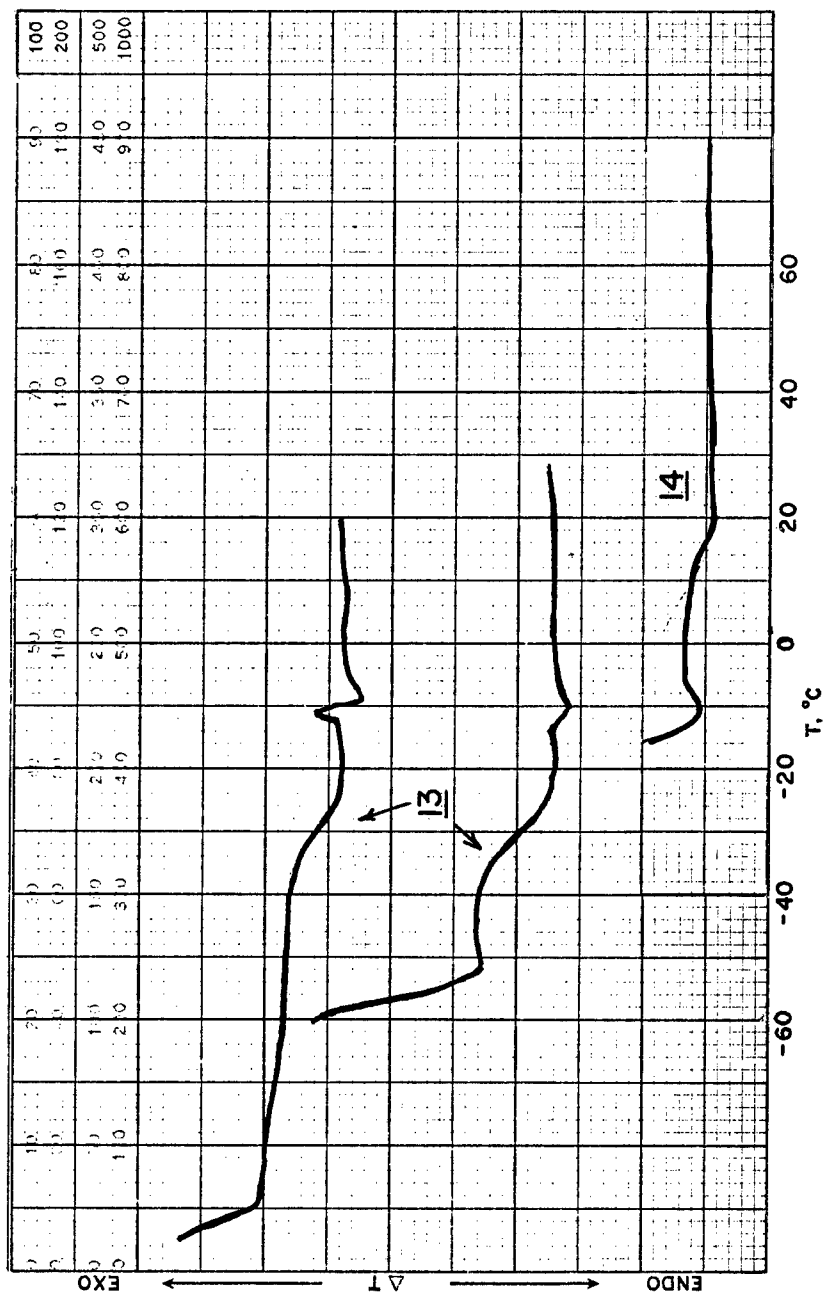
Figure 1. DSC Thermograms of Polymers 13 and 14.

61
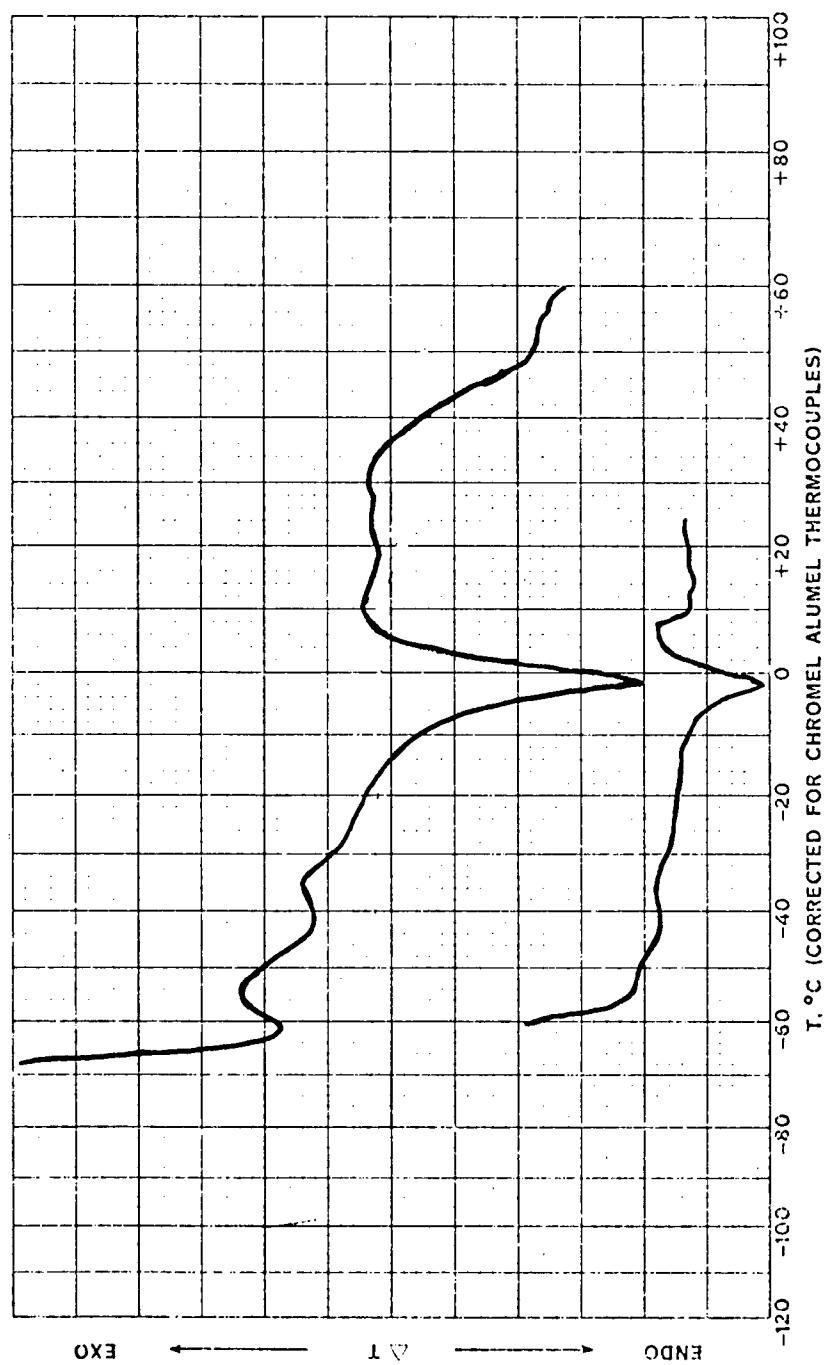
Figure 2. DSC Thermogram of Polymer 16.
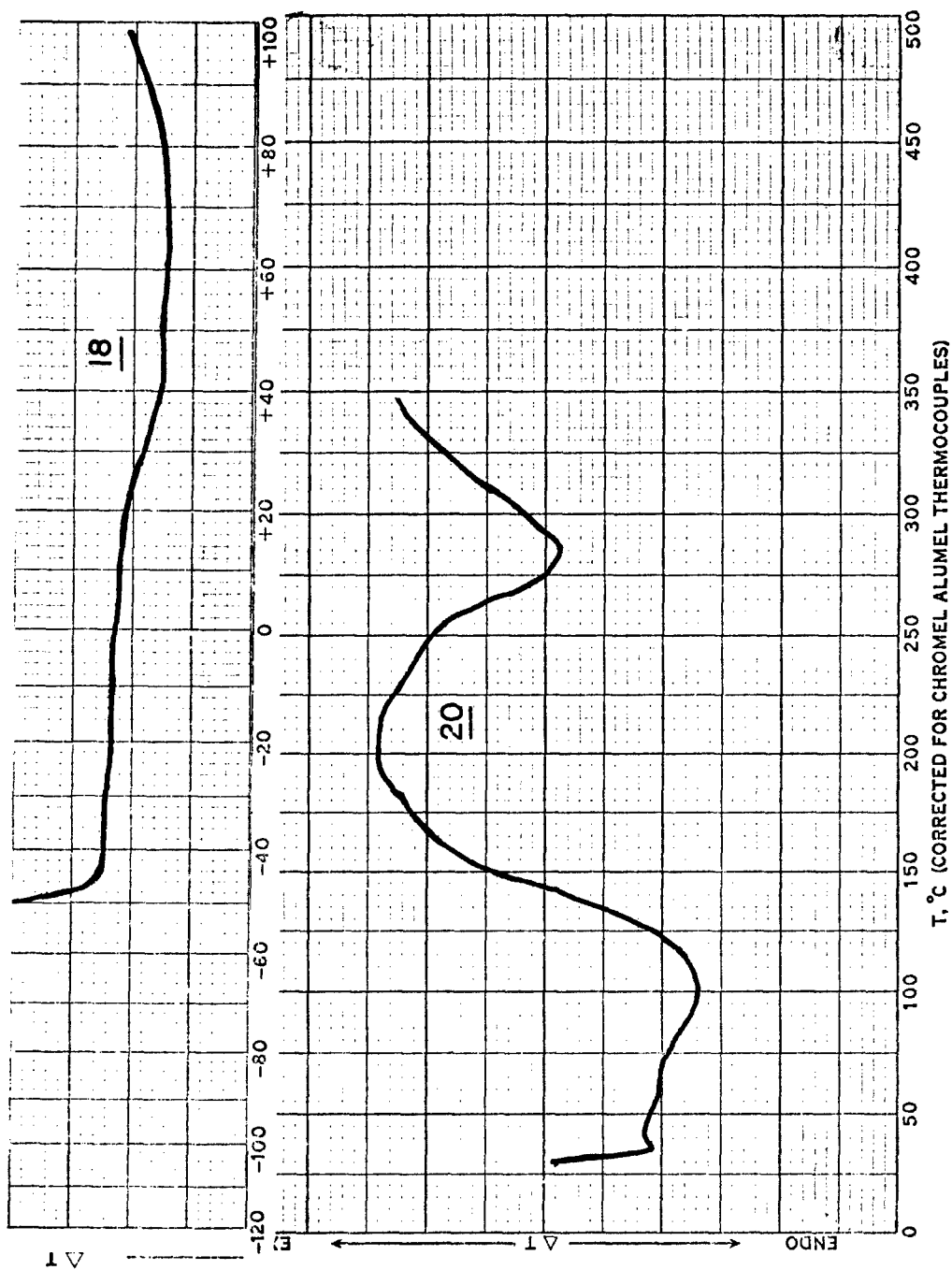
Figure 3. DSC Thermograms of Polymers 18 and 20.
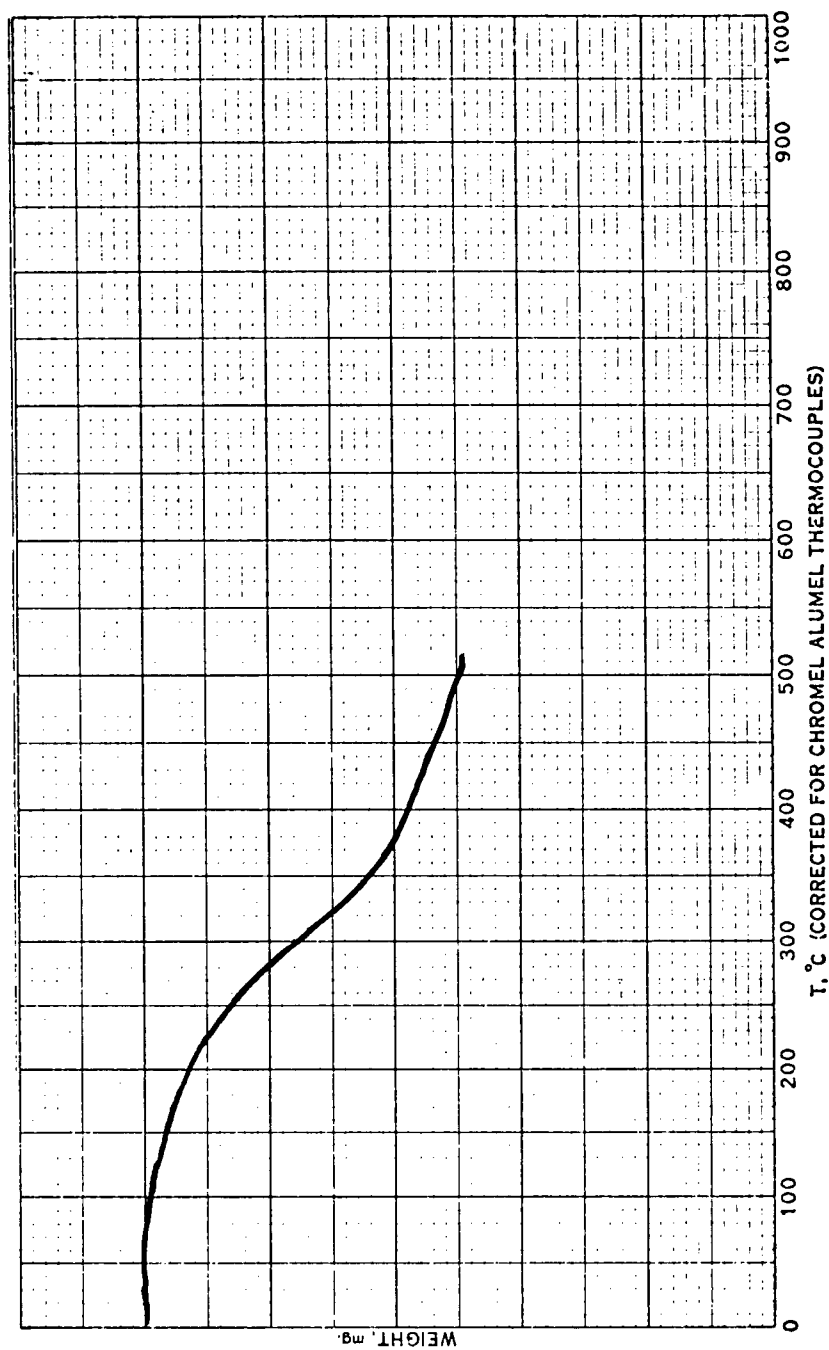
Figure 4.   TGA Thermogram of Polymer 20 (Air).
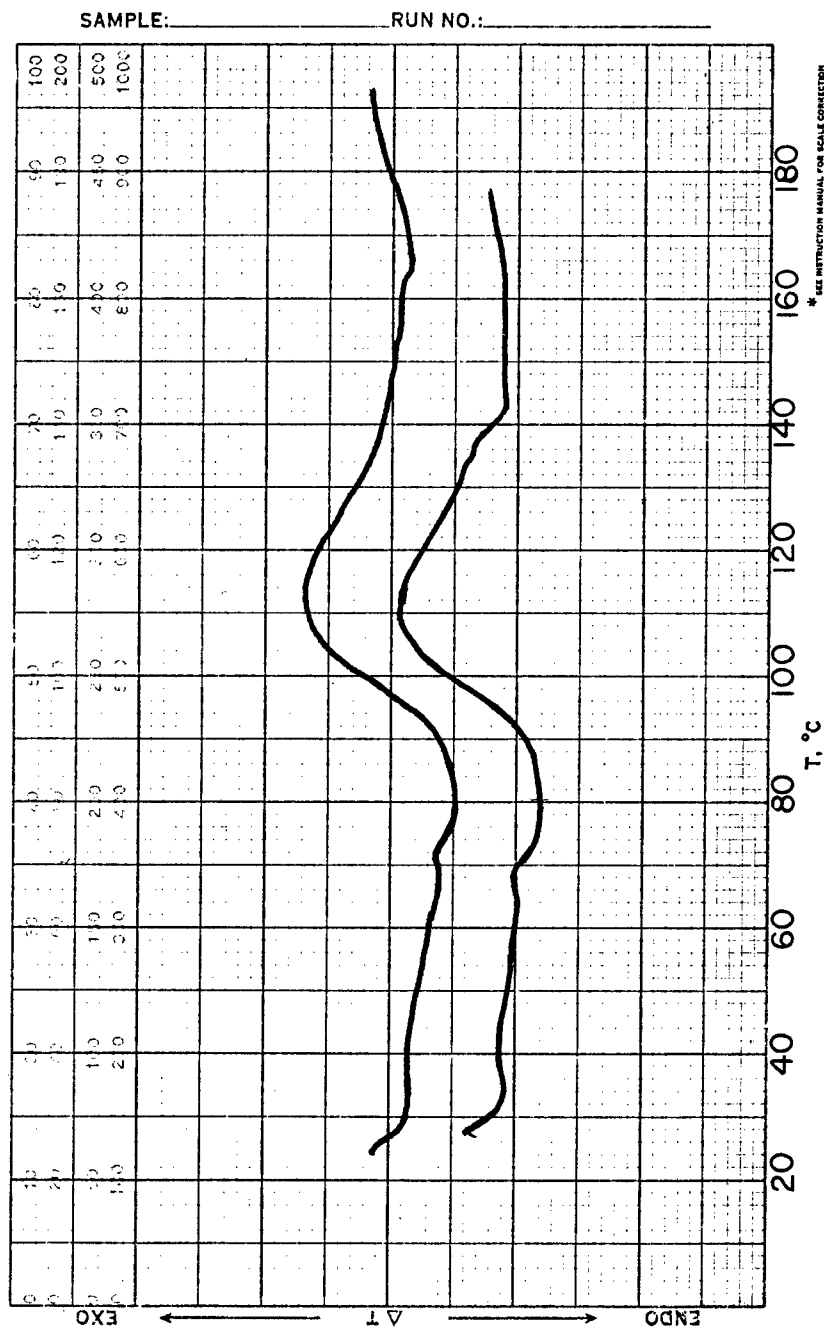
Figure 5. DSC Thermogram of Polymer 21.

65
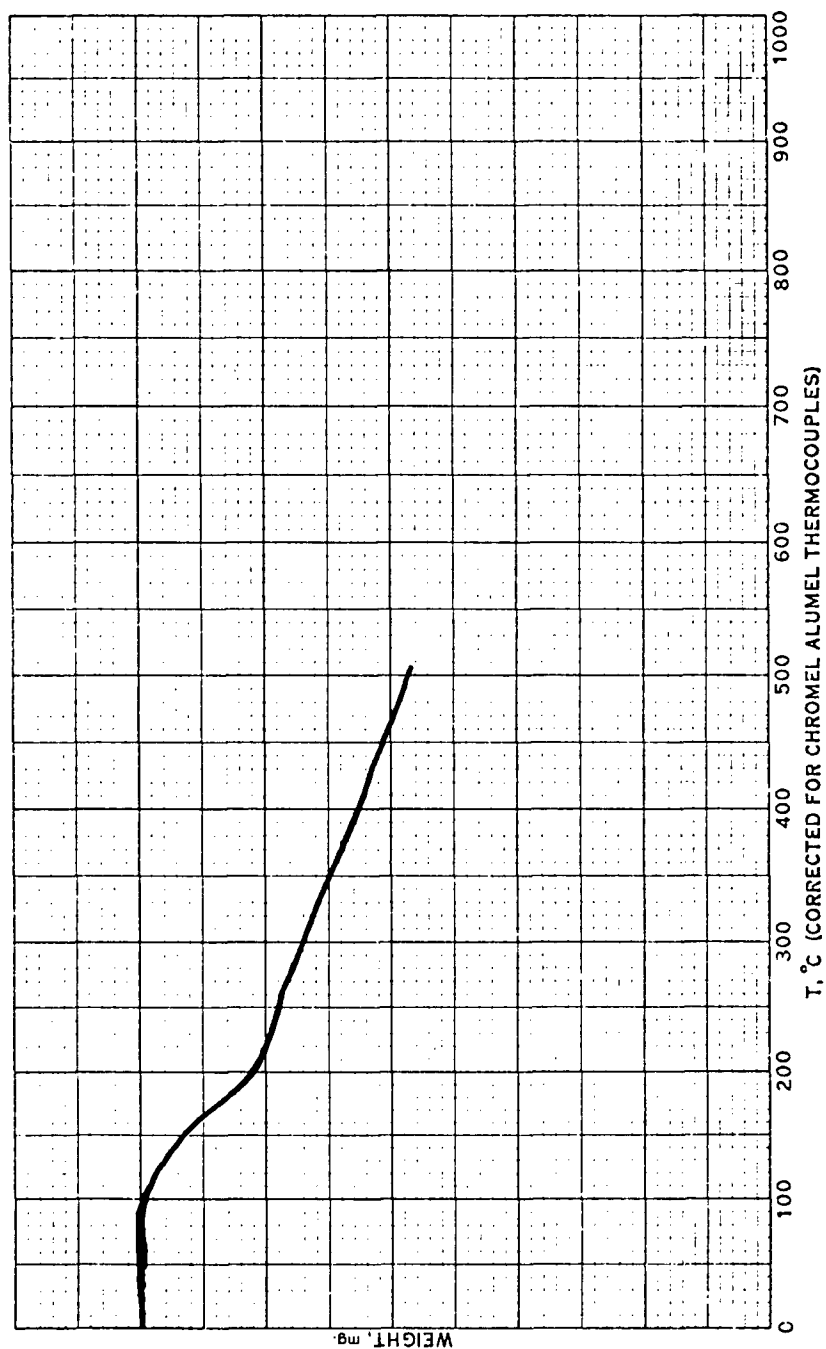
Figure 6. TGA Thermogram of Polymer 21 (Air).
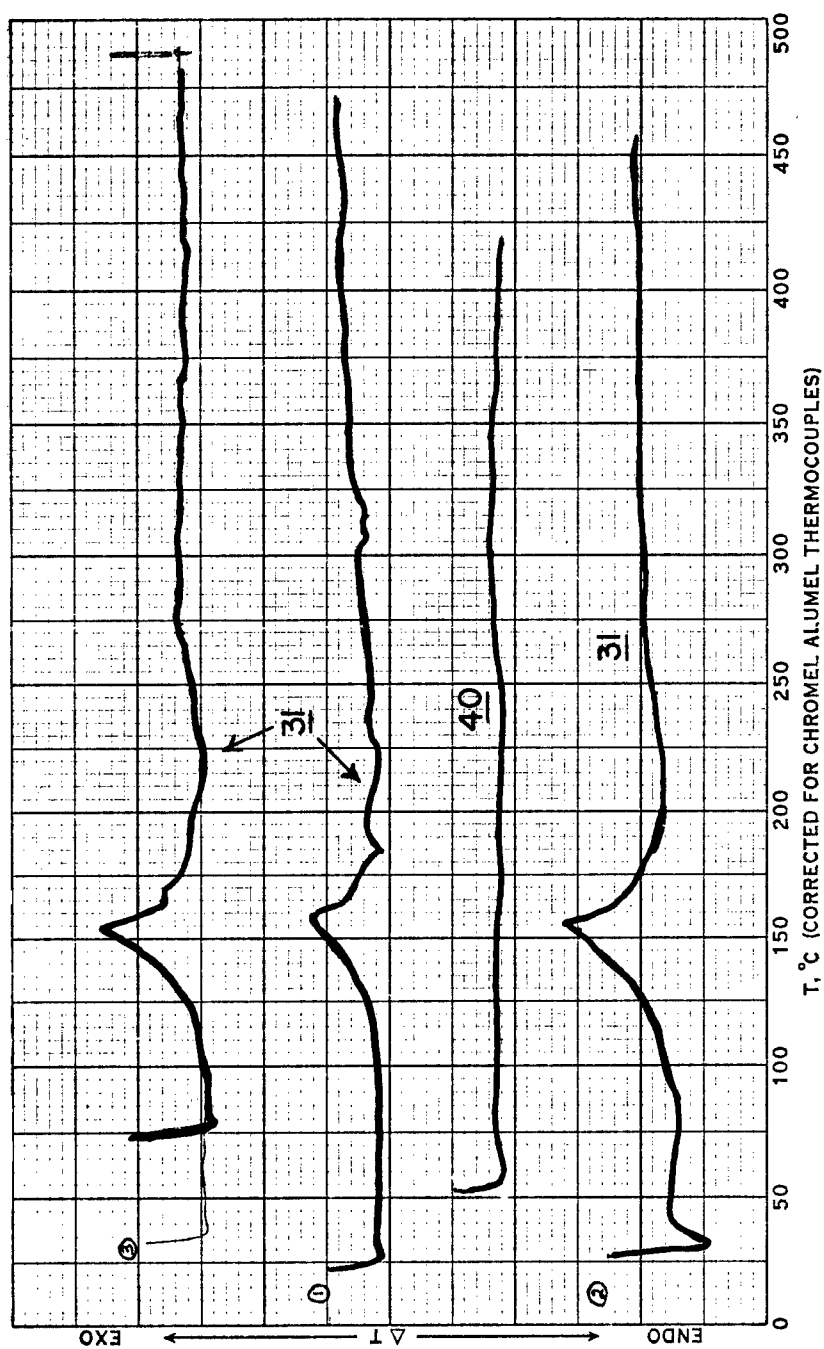
Figure 7. DSC Thermograms of Polymers 31 and 40.
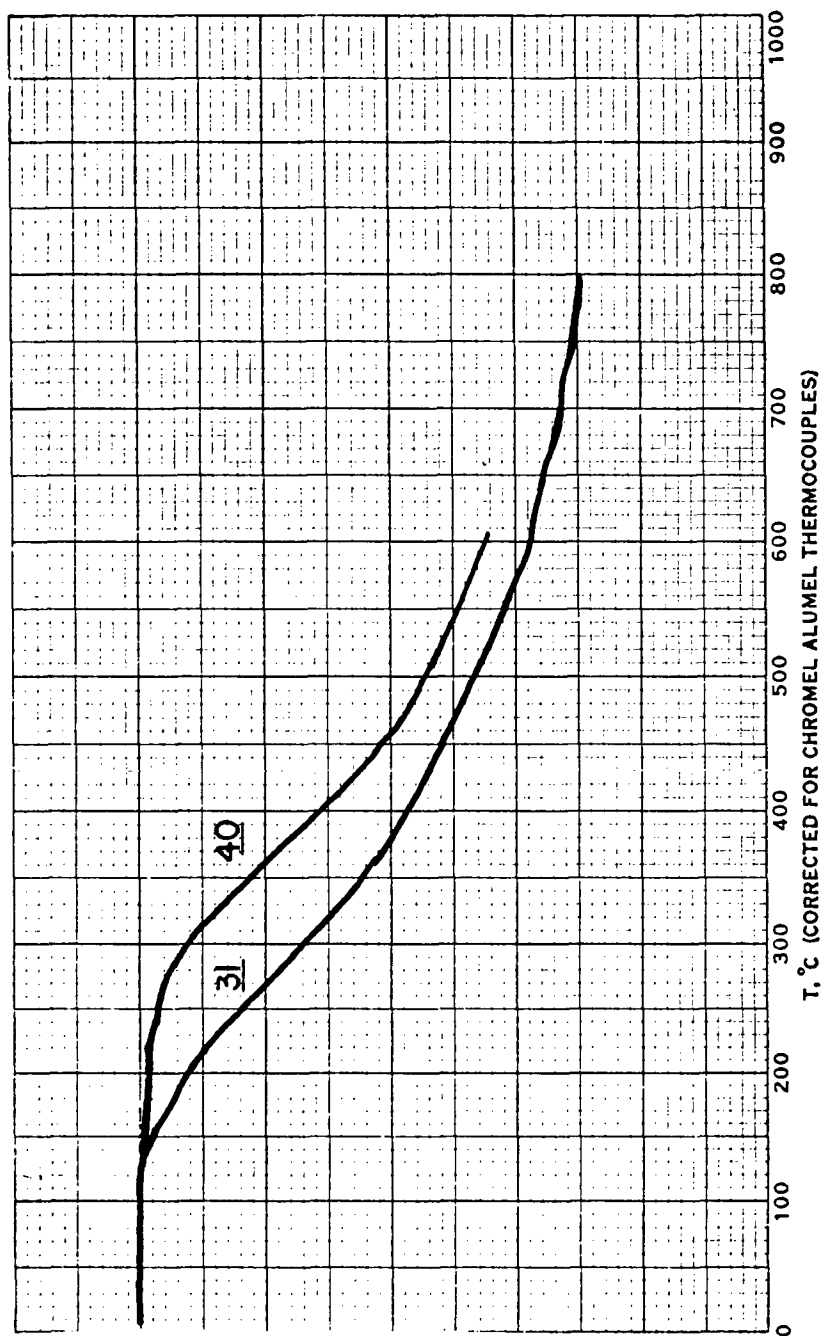
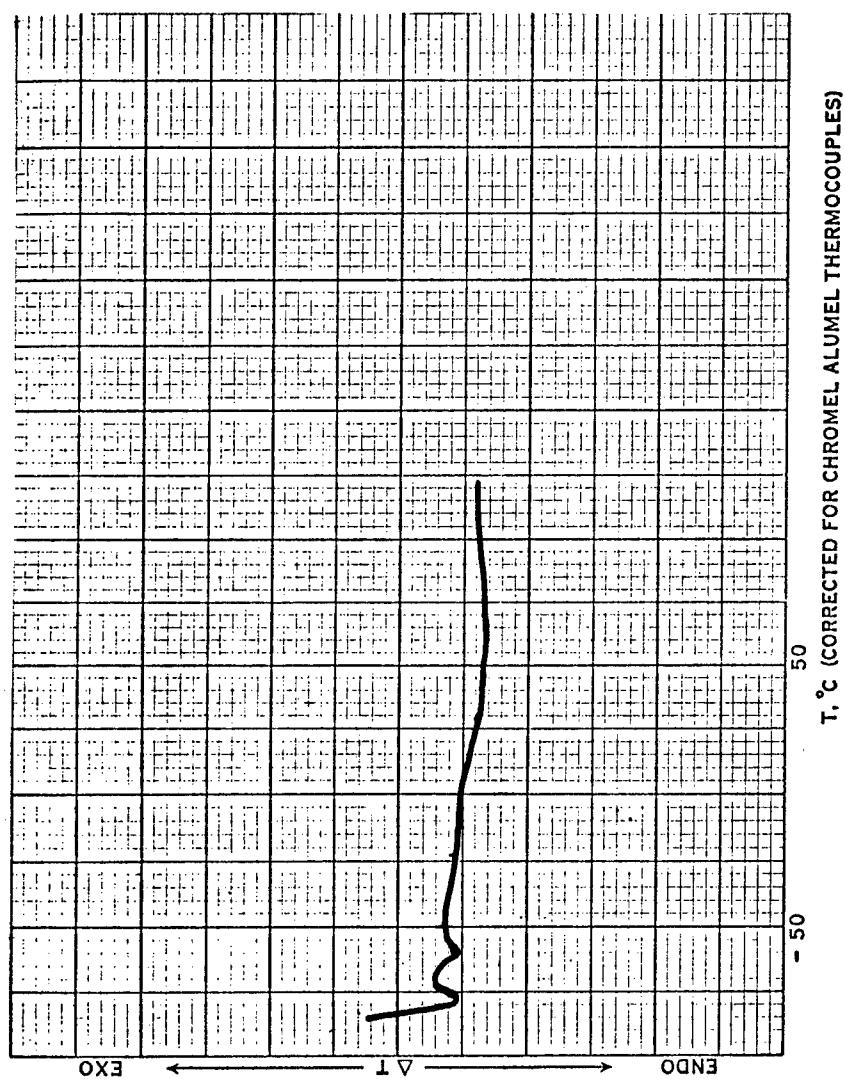Figure 8. TGA Thermograms of Polymers 31 and 40 (Nitrogen).
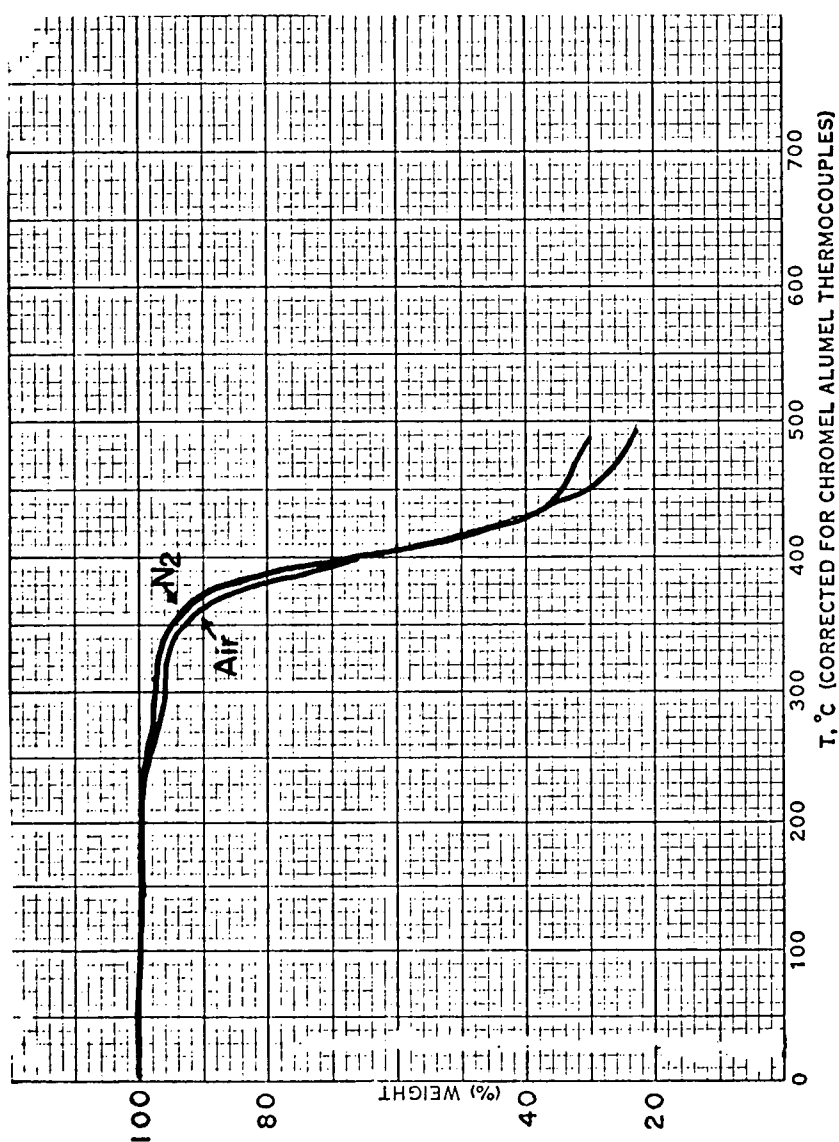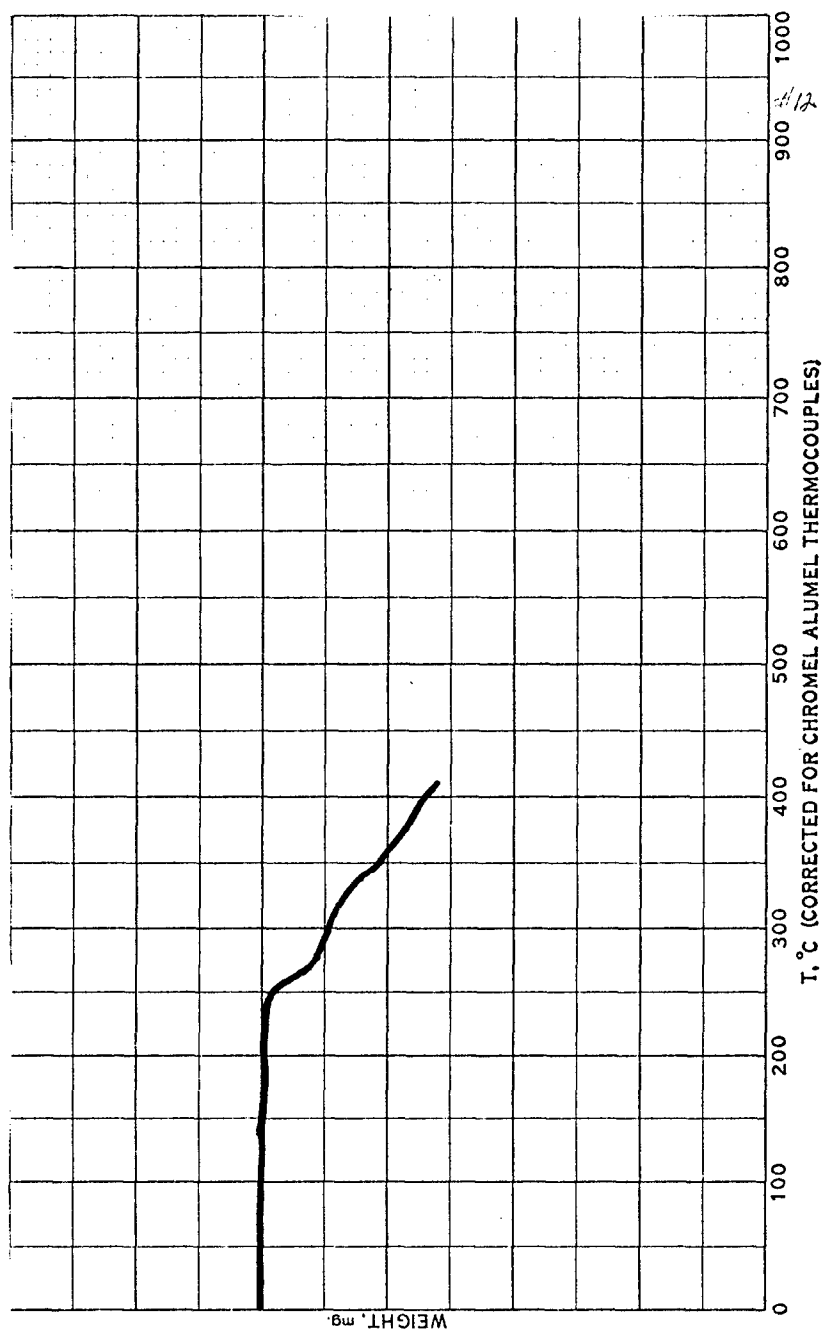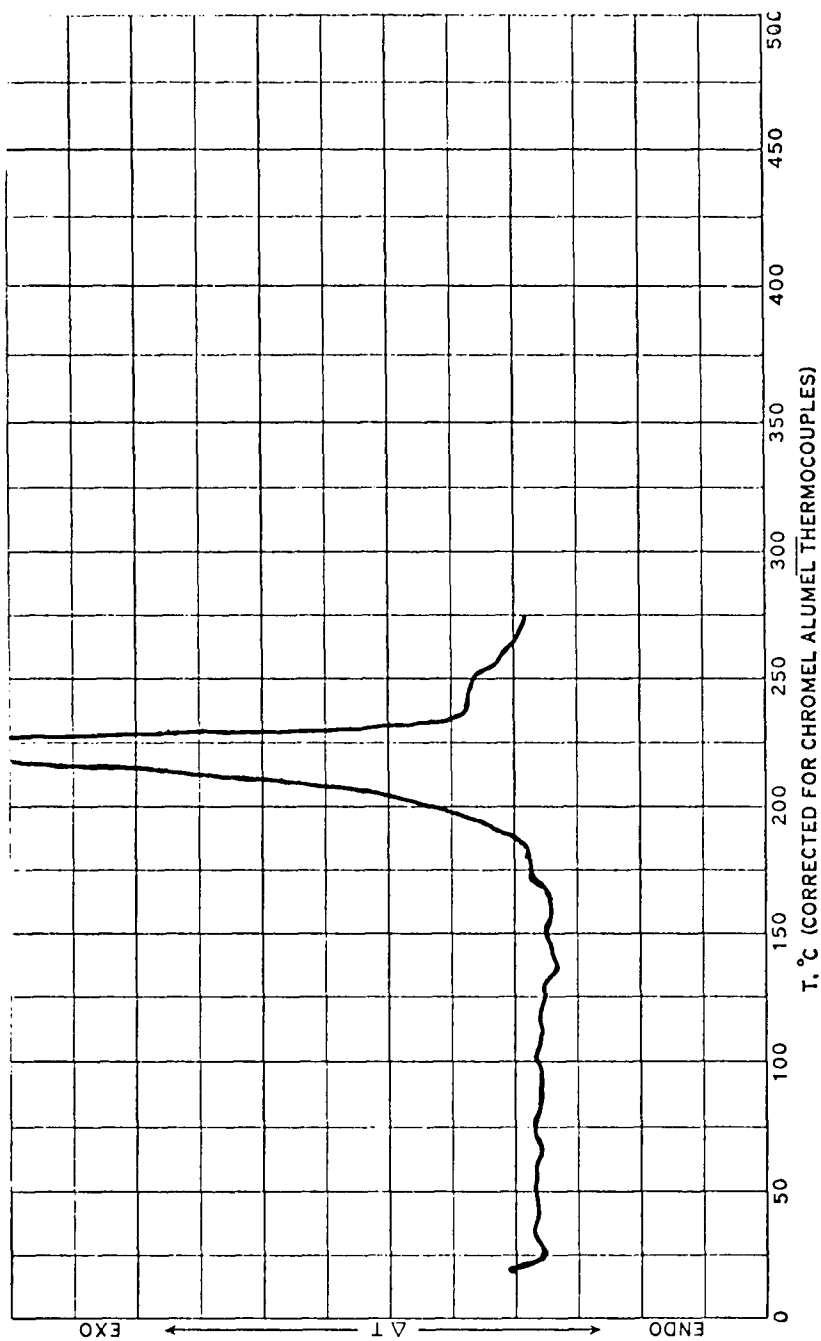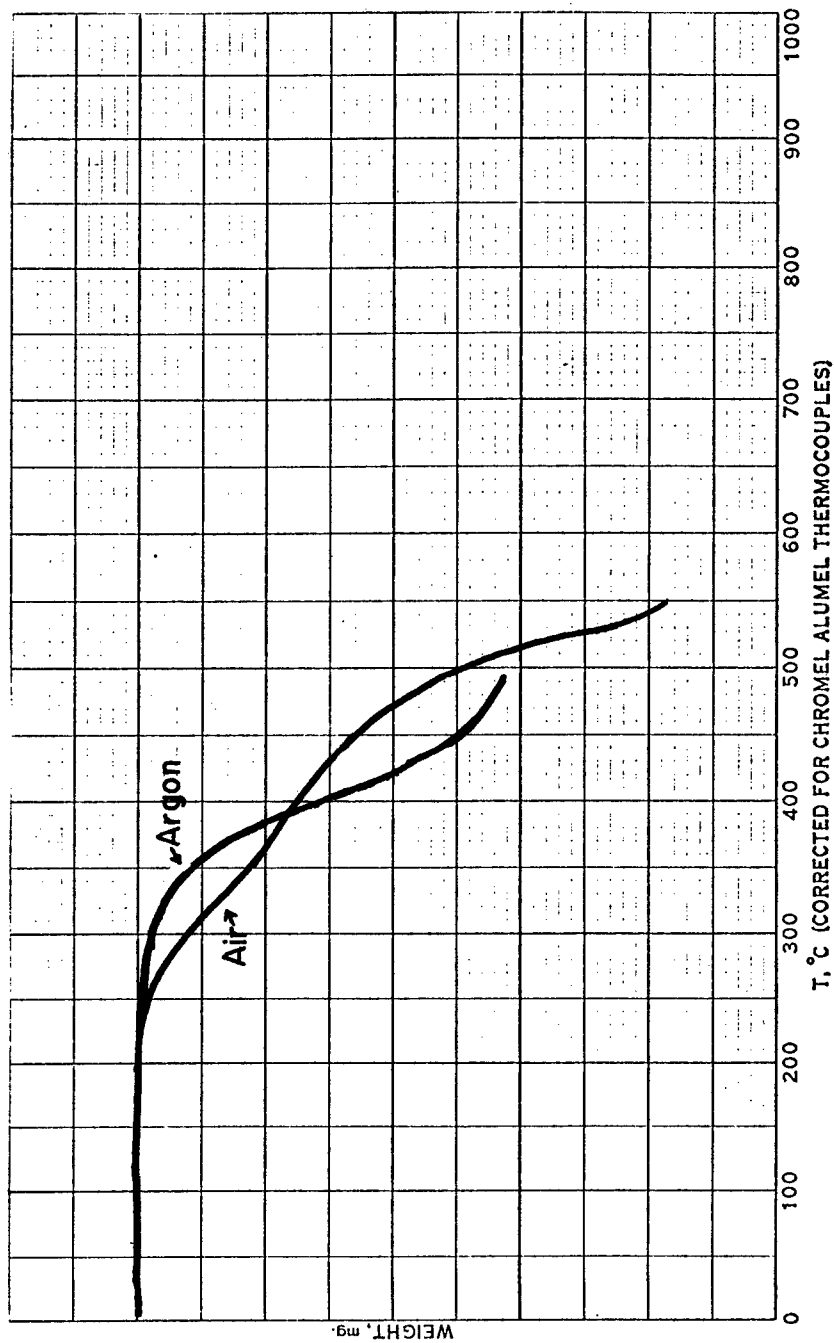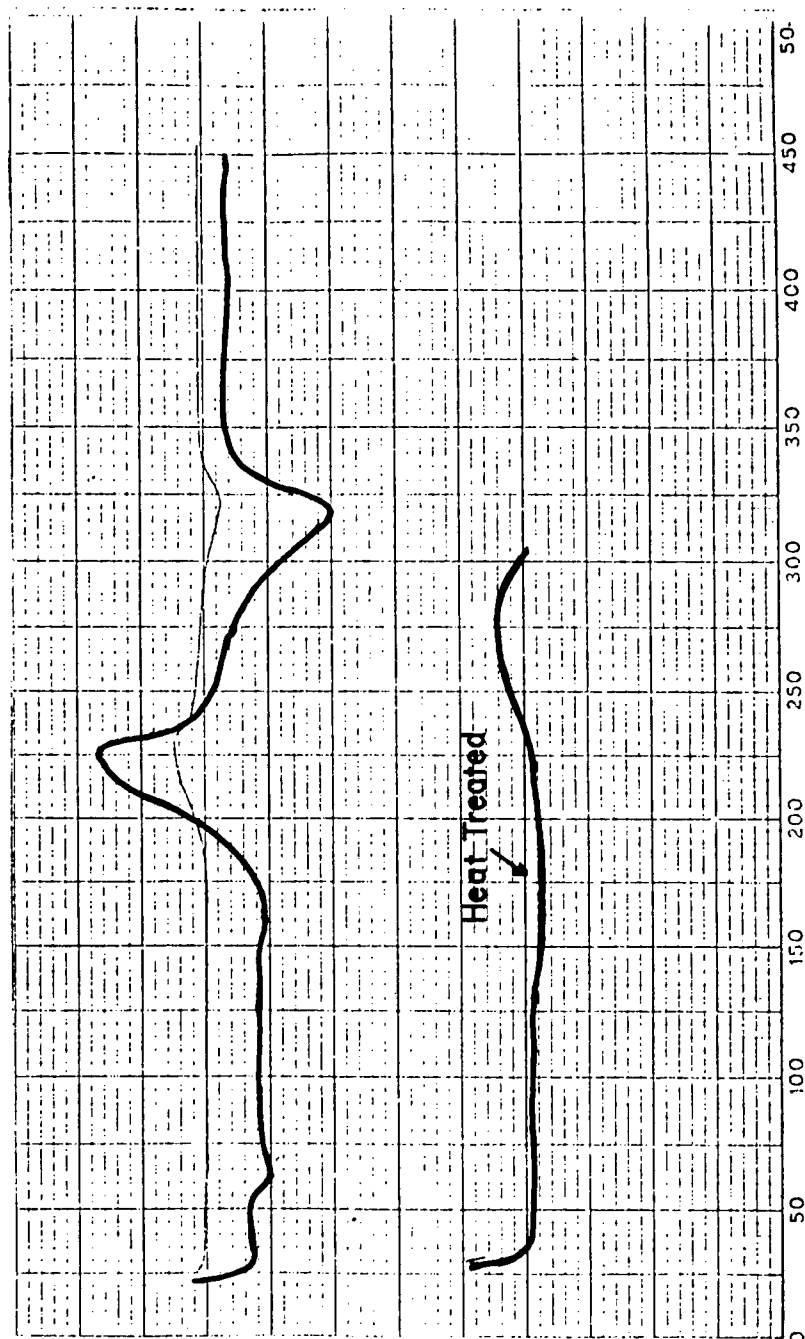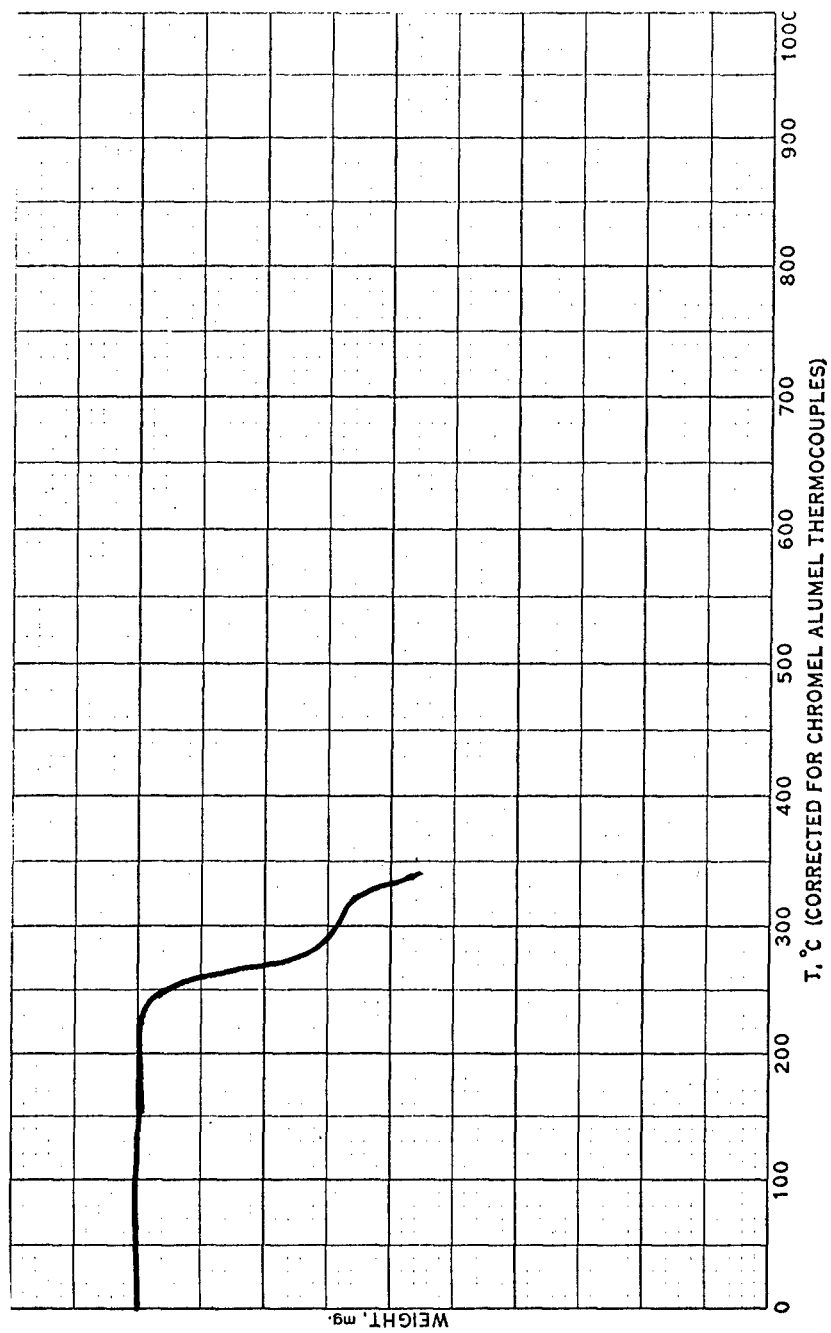
68

Figure 9.   DSC Thermogram of Polymer 44.

Figure 10. TGA Thermograms of Polymer 44.

70

Figure 11. TGA Thermogram of Polymer 62 (Air).

71

Figure 12. DSC Thermogram of Polymer 62.

72
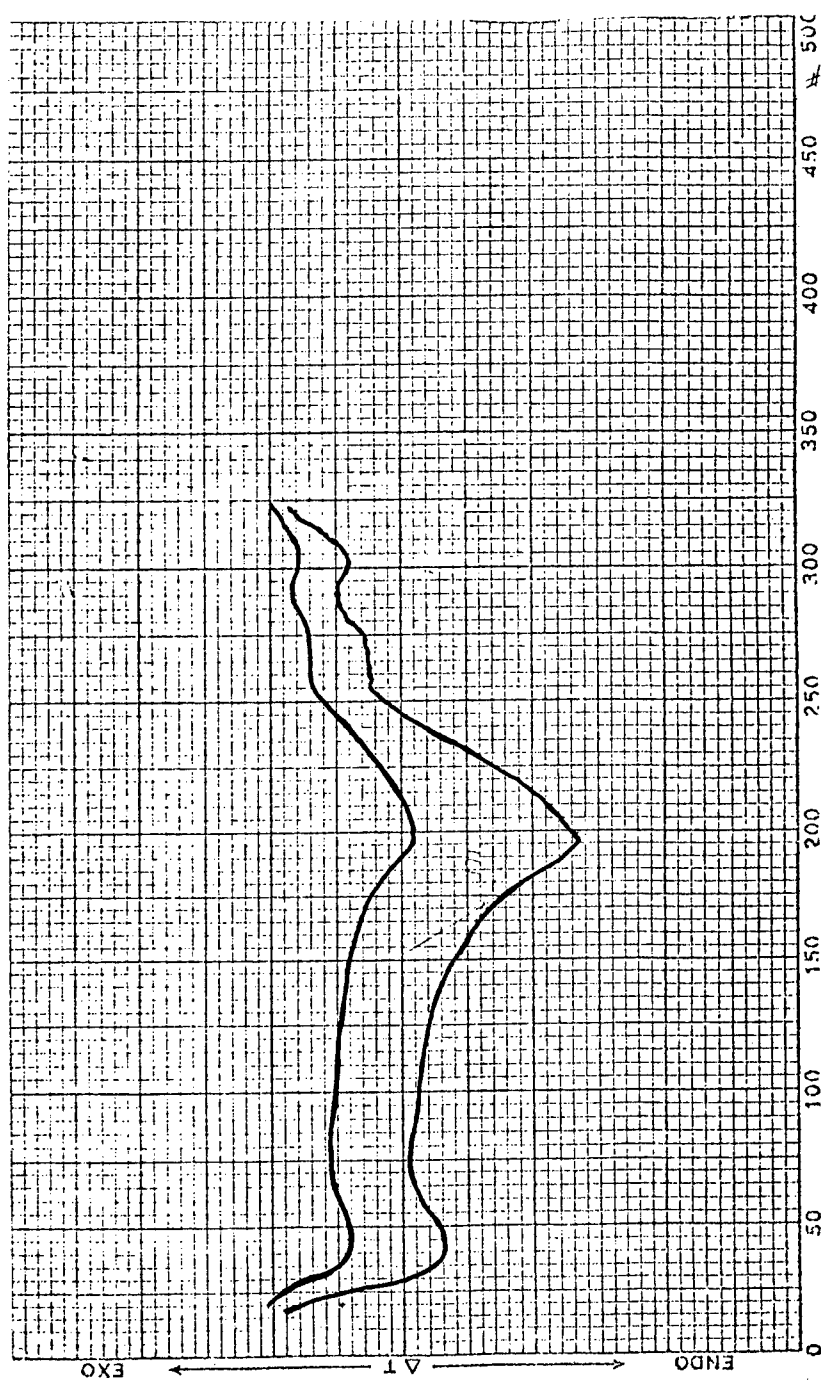
Figure 13. DSC Thermogram of Polymer 63.
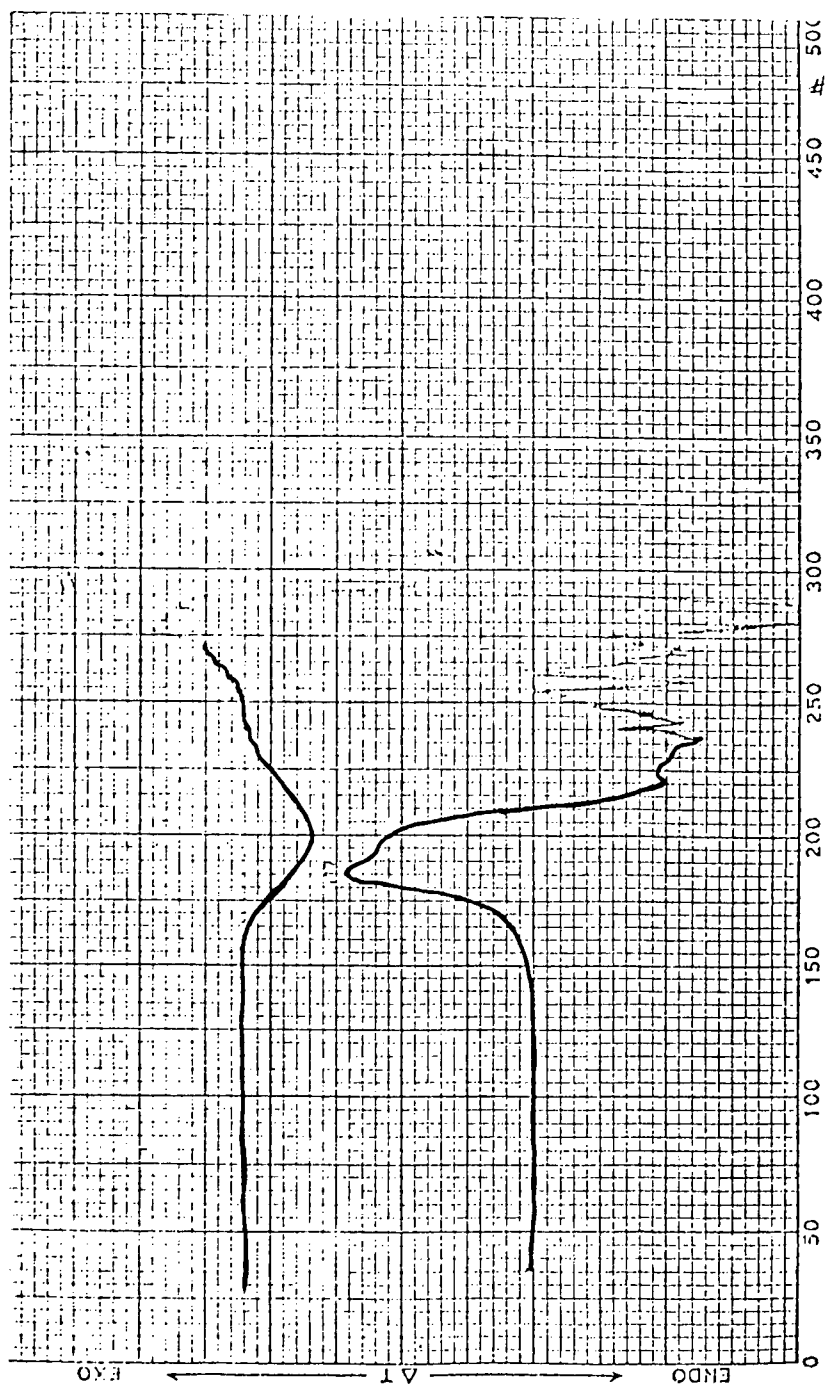
Figure 14. TMA Thermogram of Polymer 63 (Penetration Mode).

74

Figure 15. TGA Thermograms of Polymer 63.

Figure 16. DSC Thermograms of Polymers 64.

Figure 17. TGA Thermogram of Polymer 64 (Nitrogen).
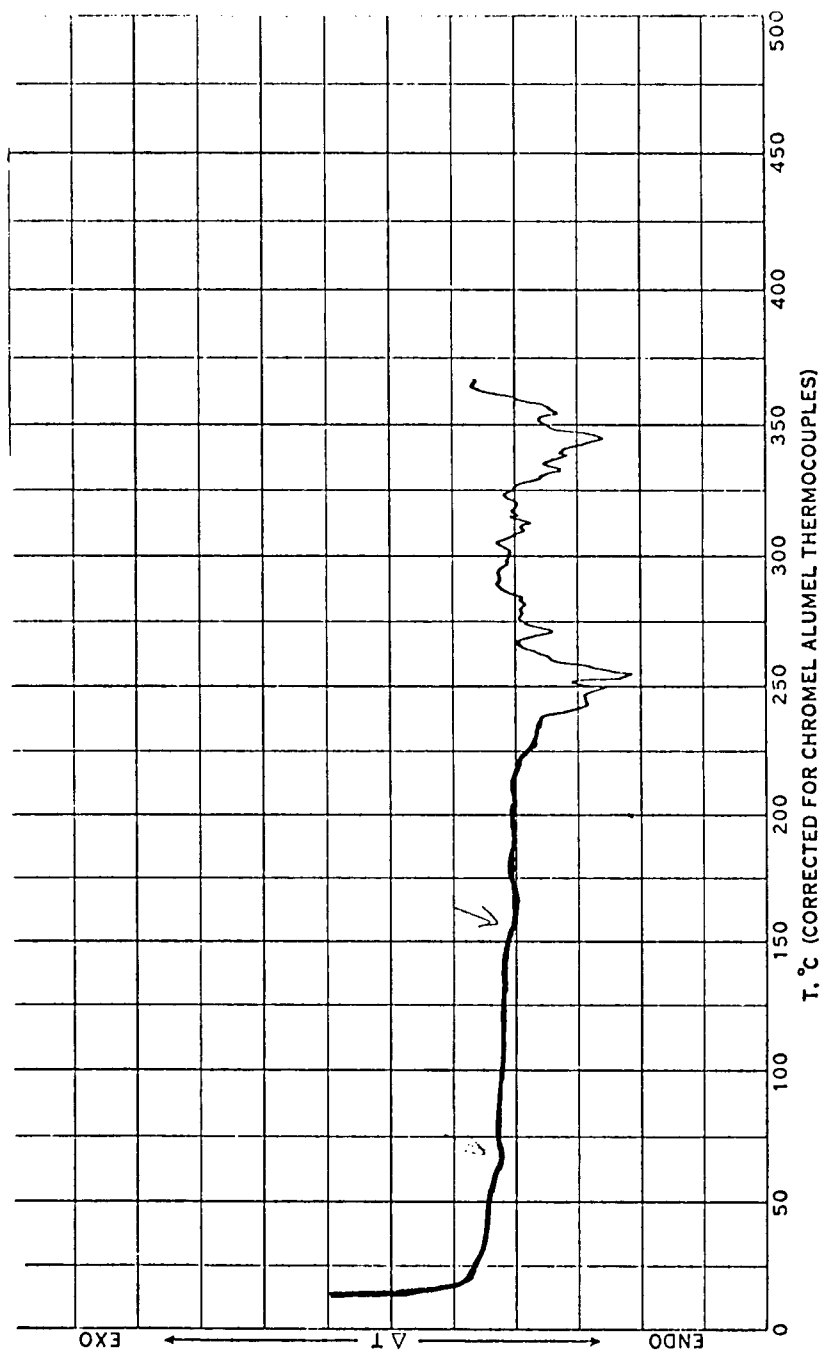
Figure 18. DSC Thermogram of Polymer 65.
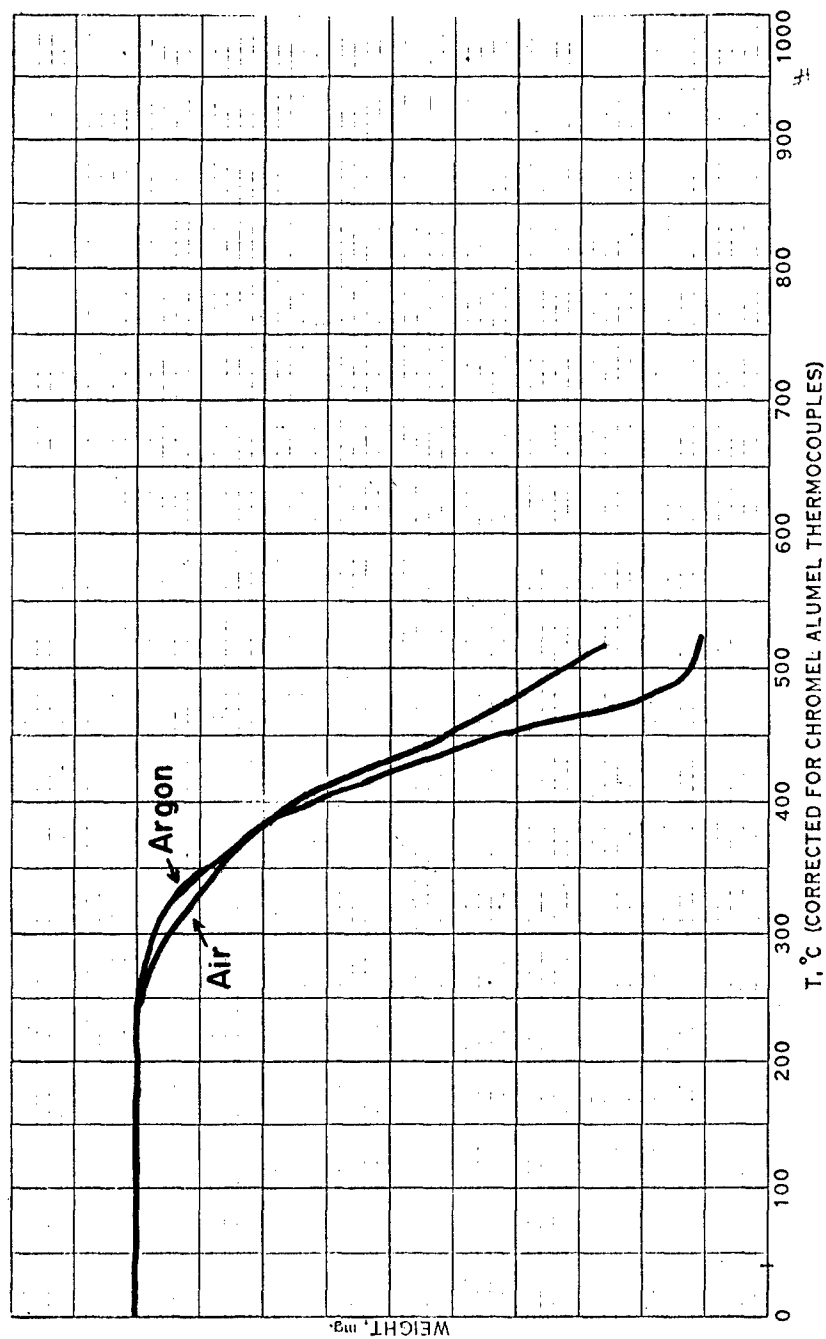
Figure 19. TGA Thermograms of Polymer 65.
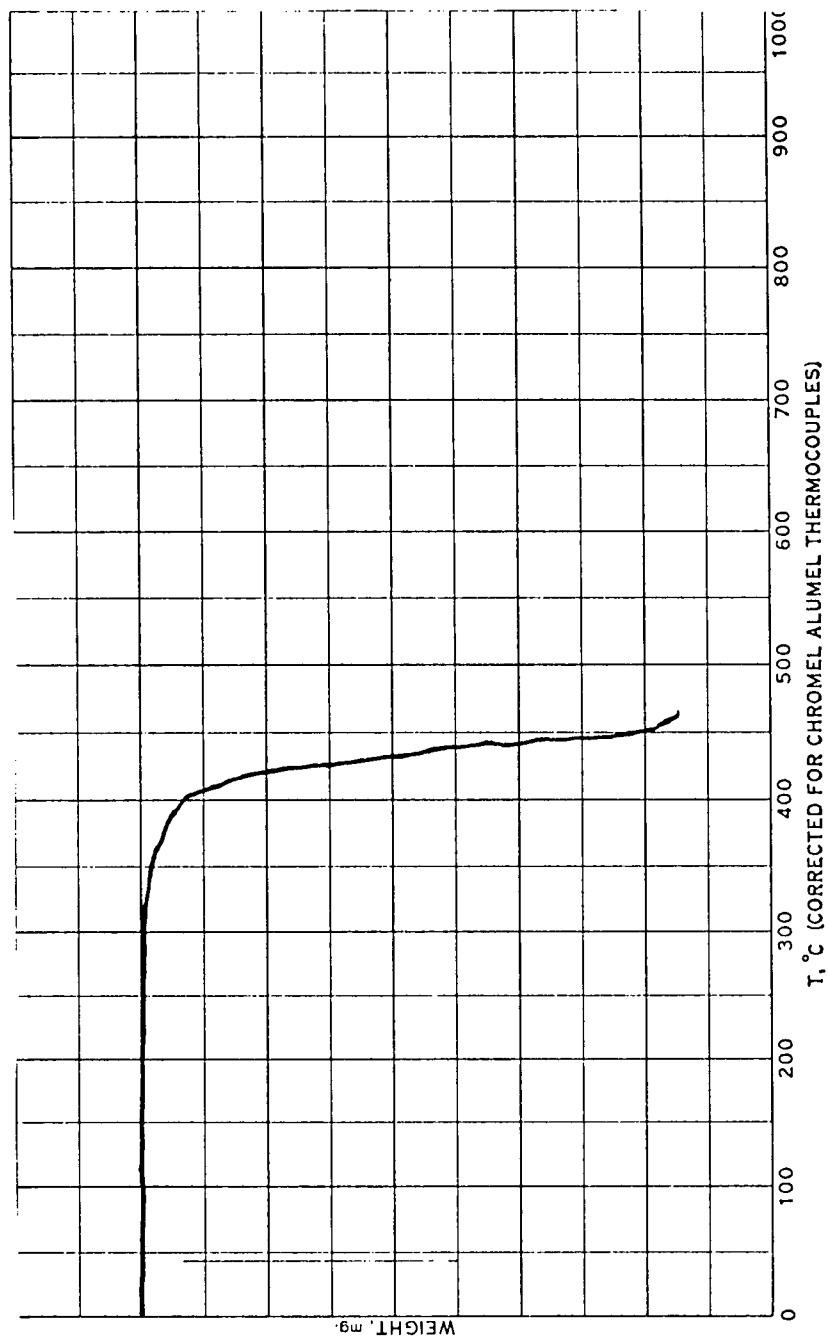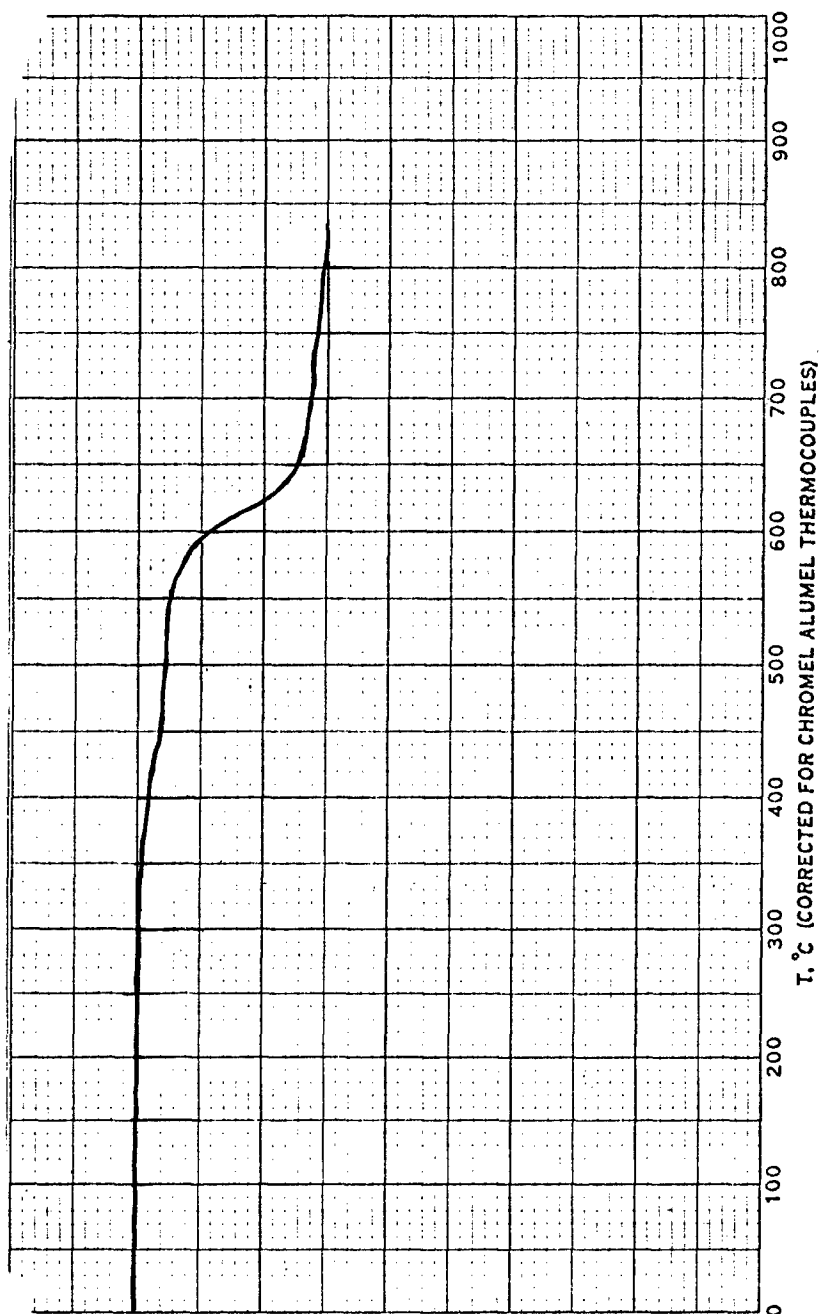
Figure 20. TGA Thermogram of Polymer 65 (Argon).

80

Figure 21. TGA Thermogram of Polymer 71 (Nitrogen).

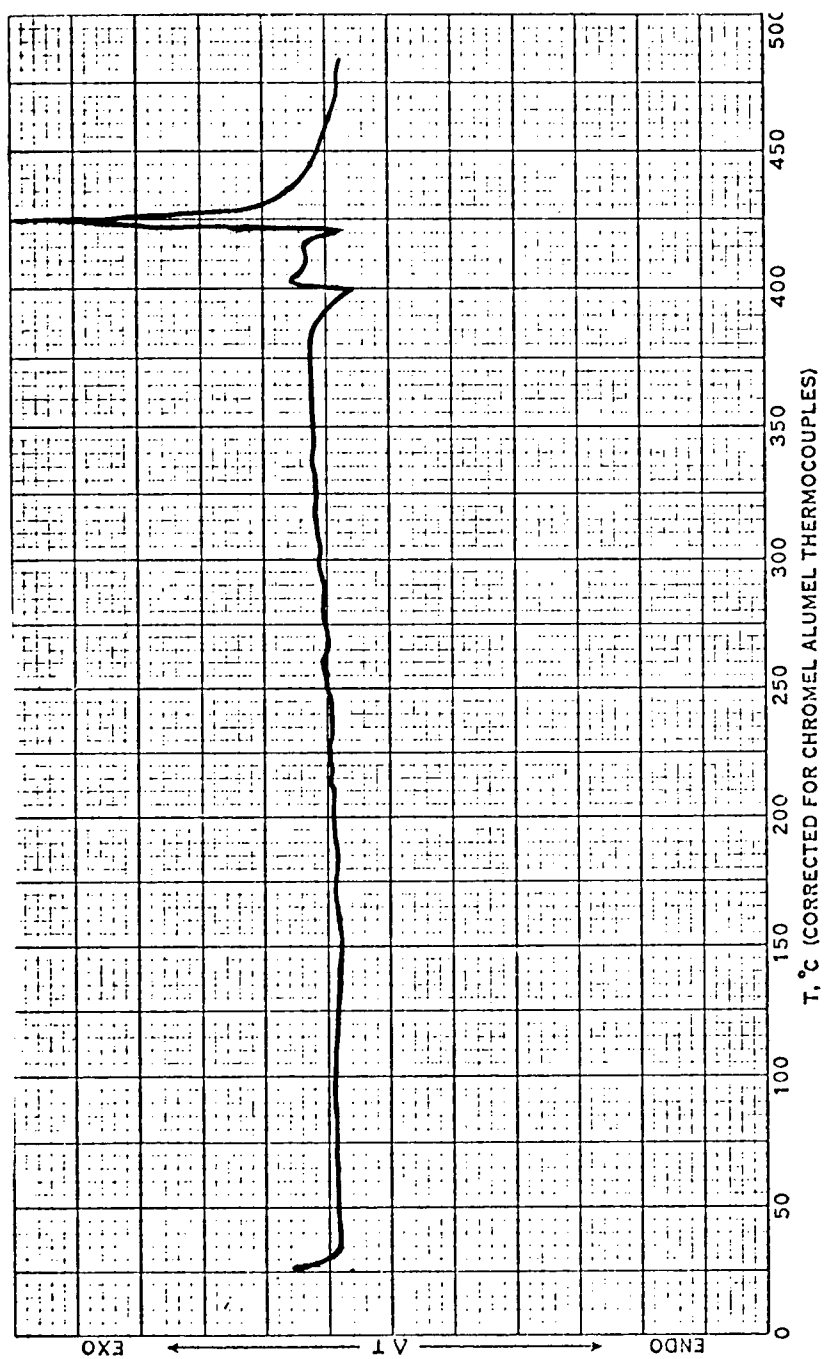T, °C (CORRECTED FOR CHROMEL ALUMEL THERMOCOUPLES)

81

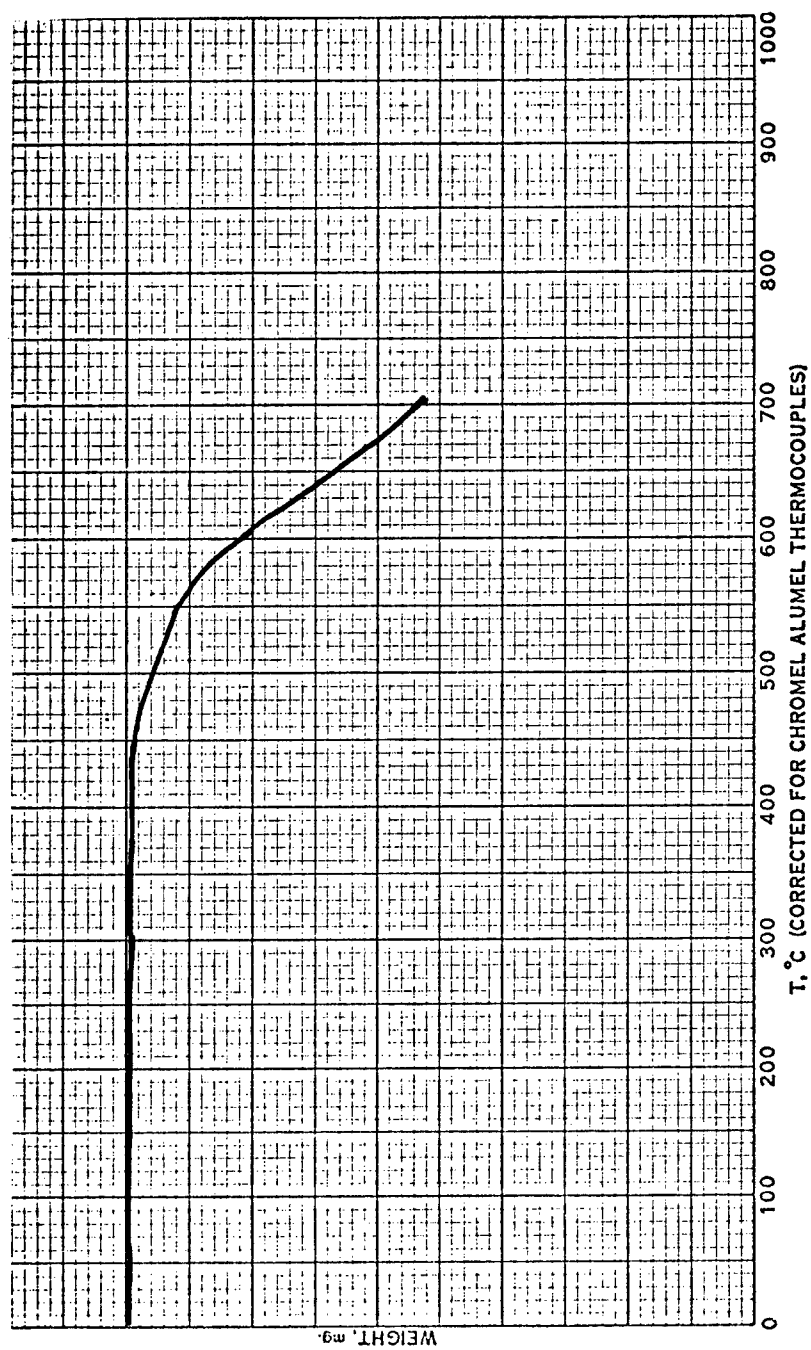Figure 22. DSC Thermogram of Model Compound 98.

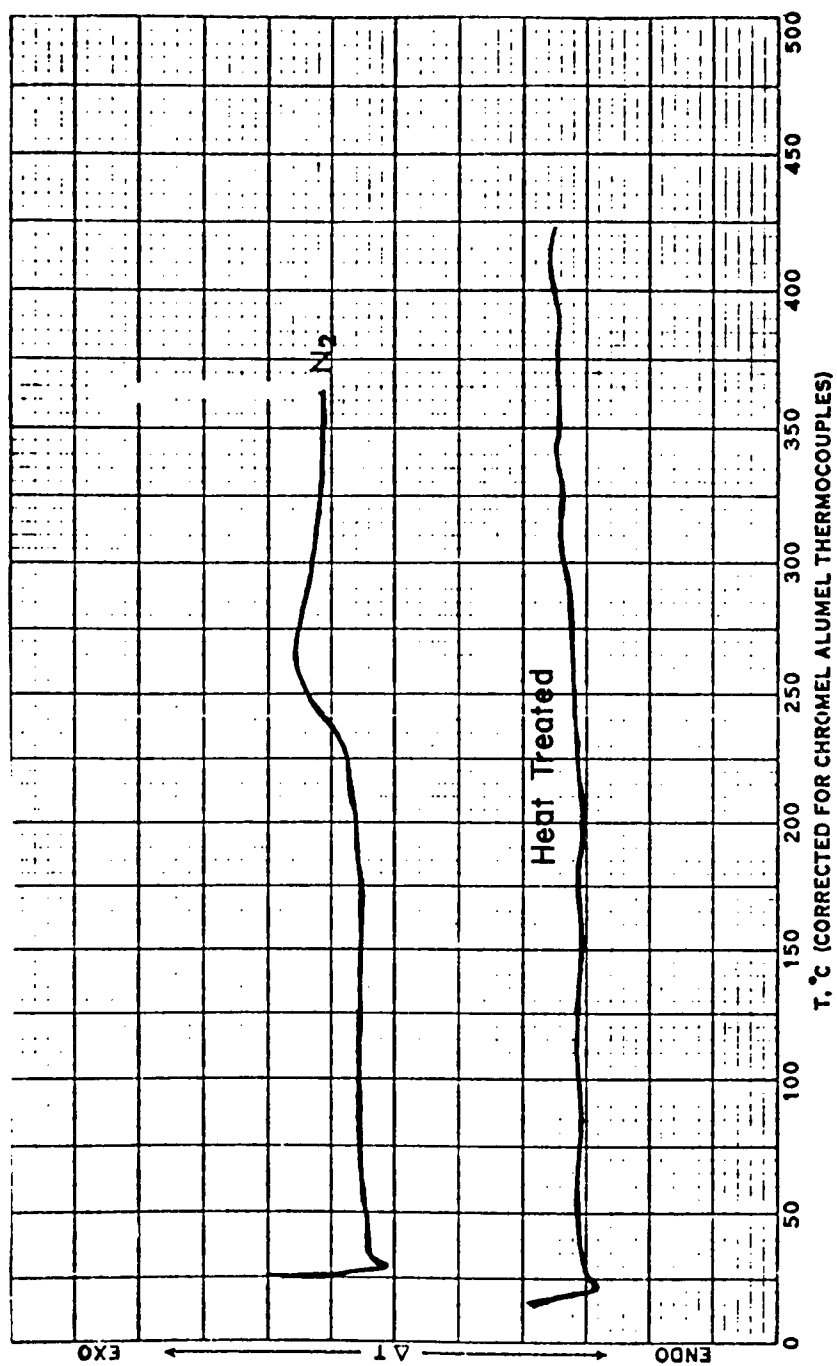Figure 23. TGA Thermogram of Model Compound 98.

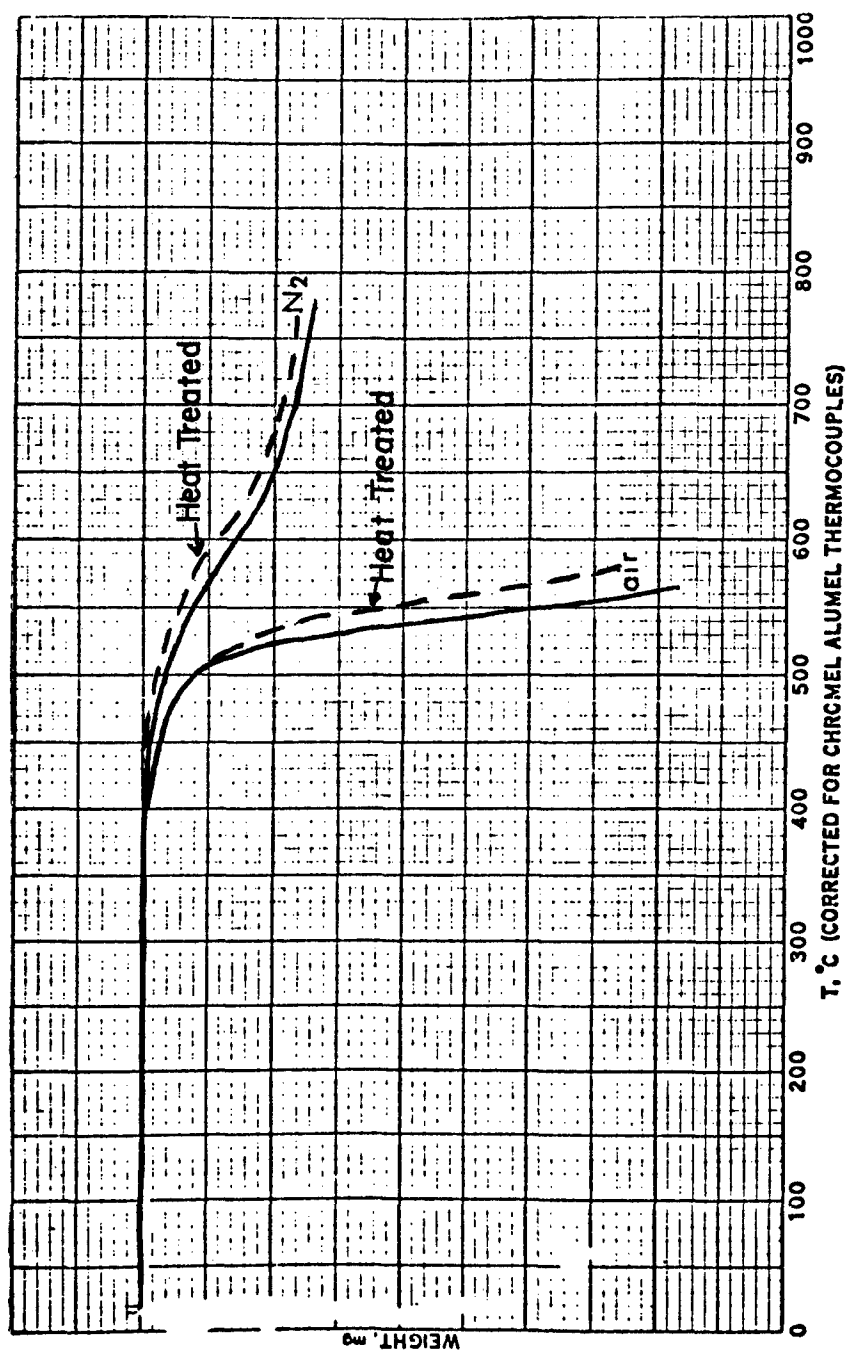Figure 24. DSC Thermograms of Polymer 101.

84

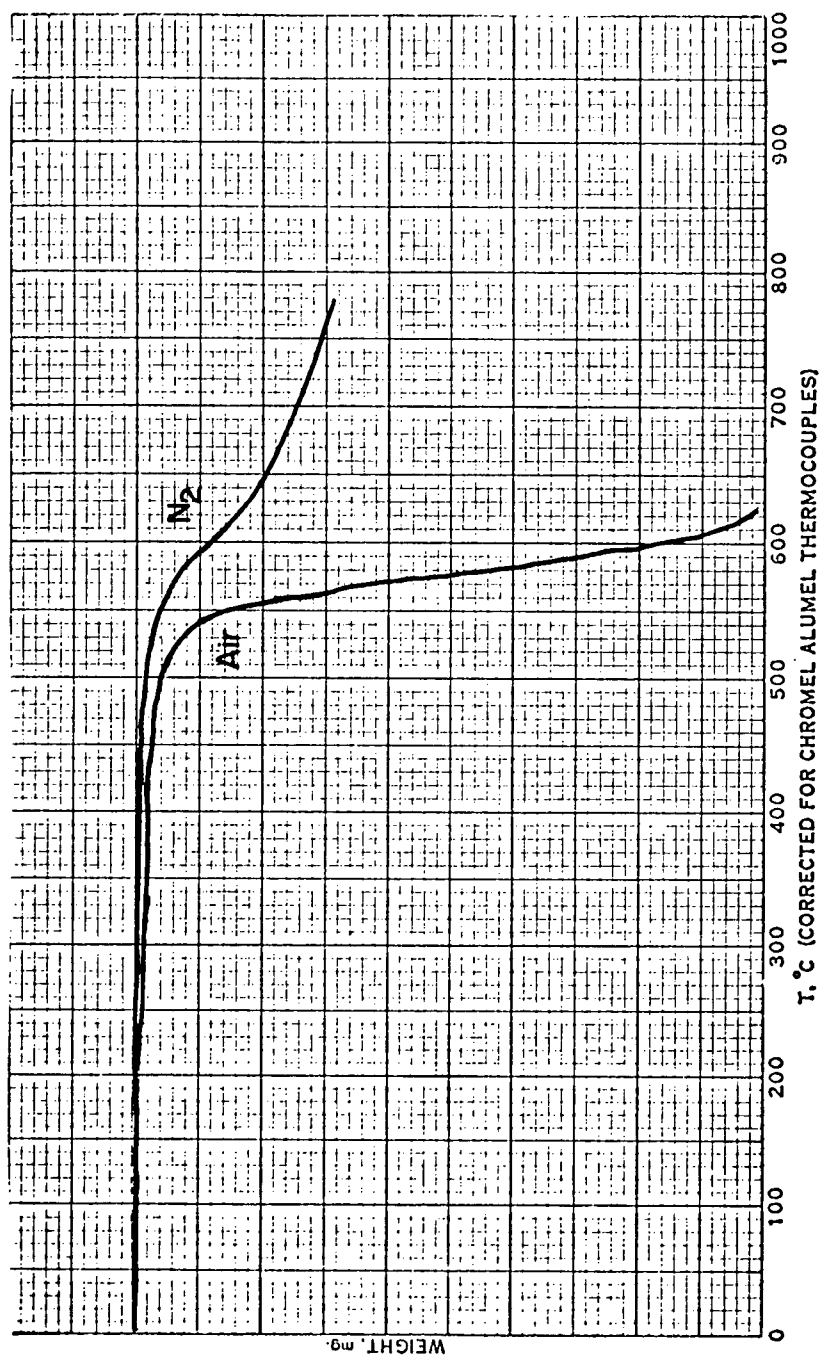Figure 25. TGA Thermograms of Polymer 101.
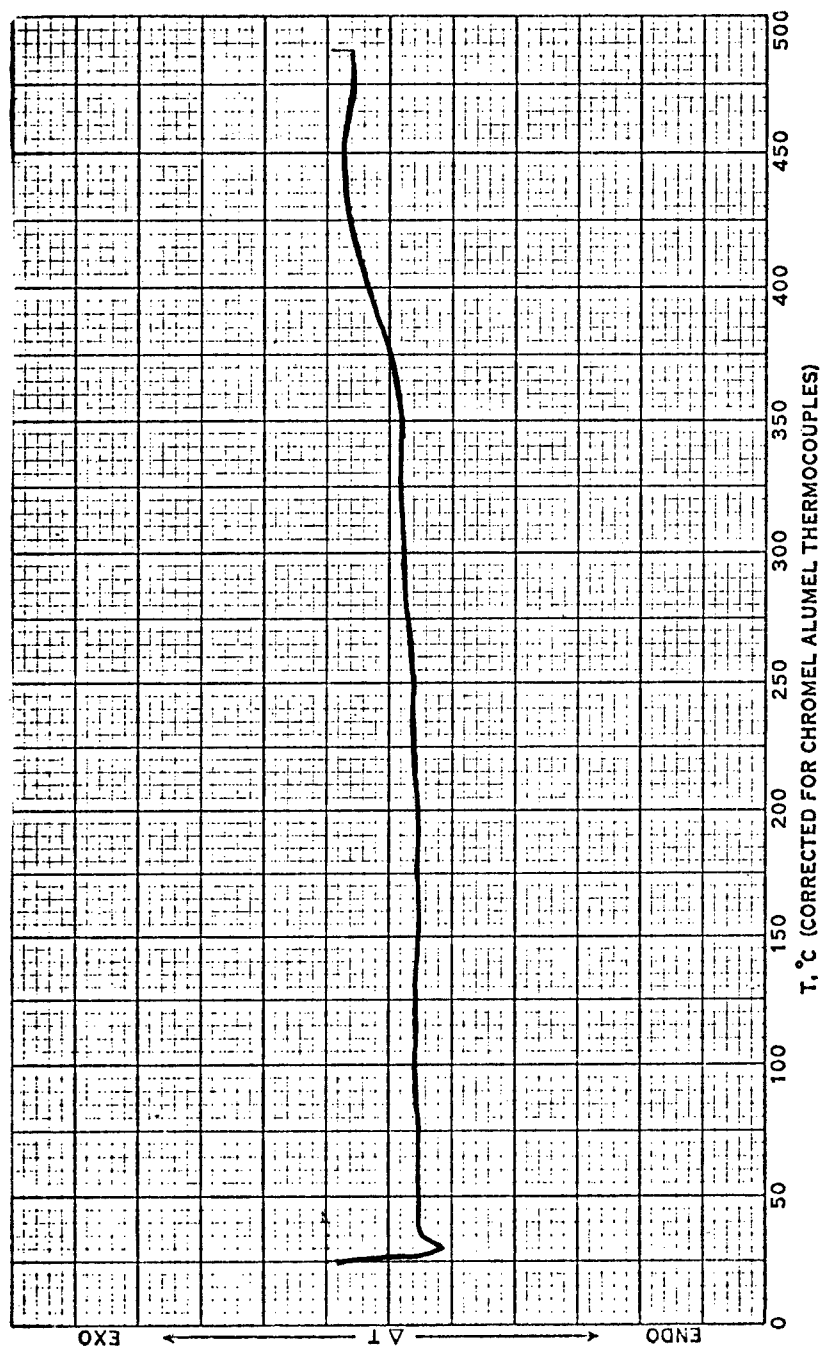
Figure 26. TGA Thermograms of Polymer 102.

Figure 27. DSC Thermogram of Polymer 102.

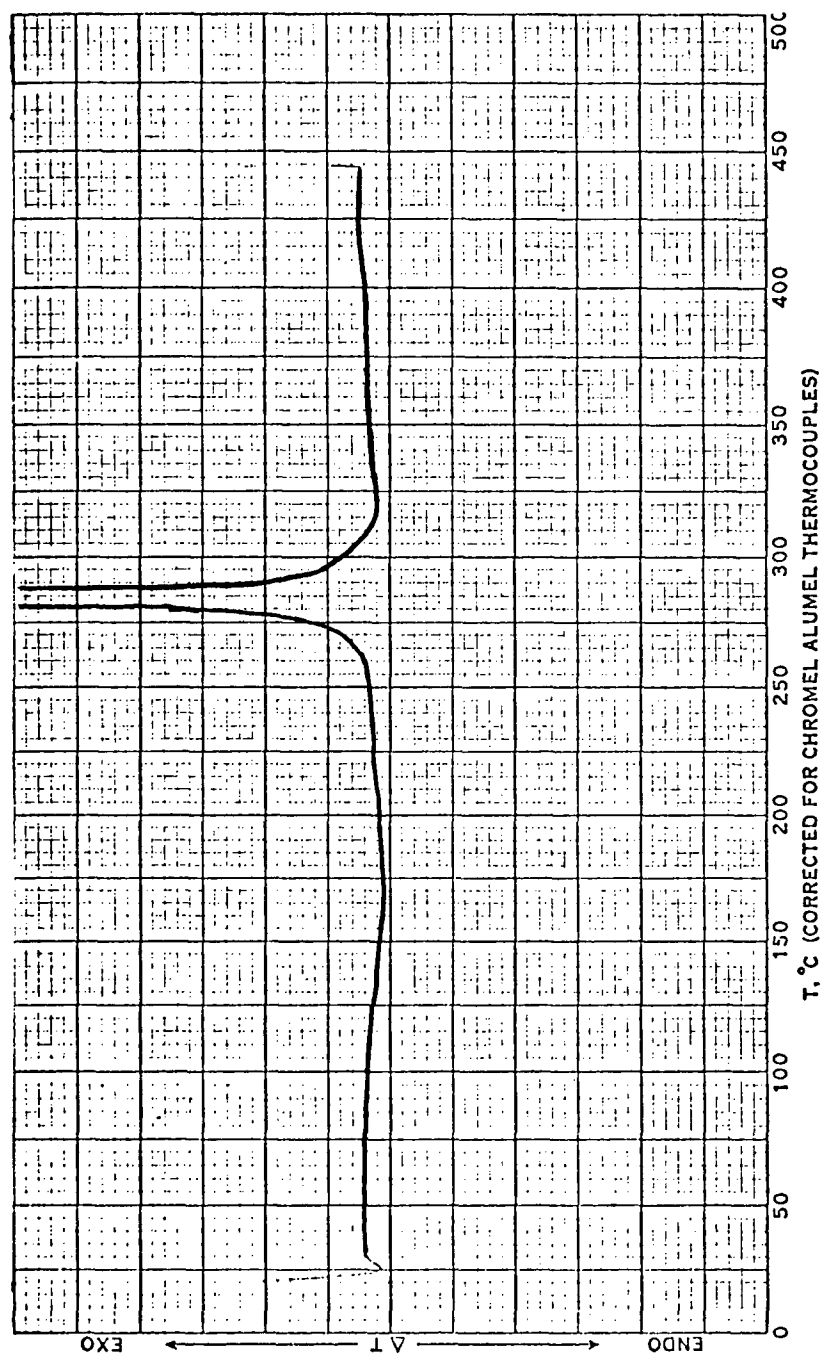Figure 28. DSC Thermogram of Compound 105.

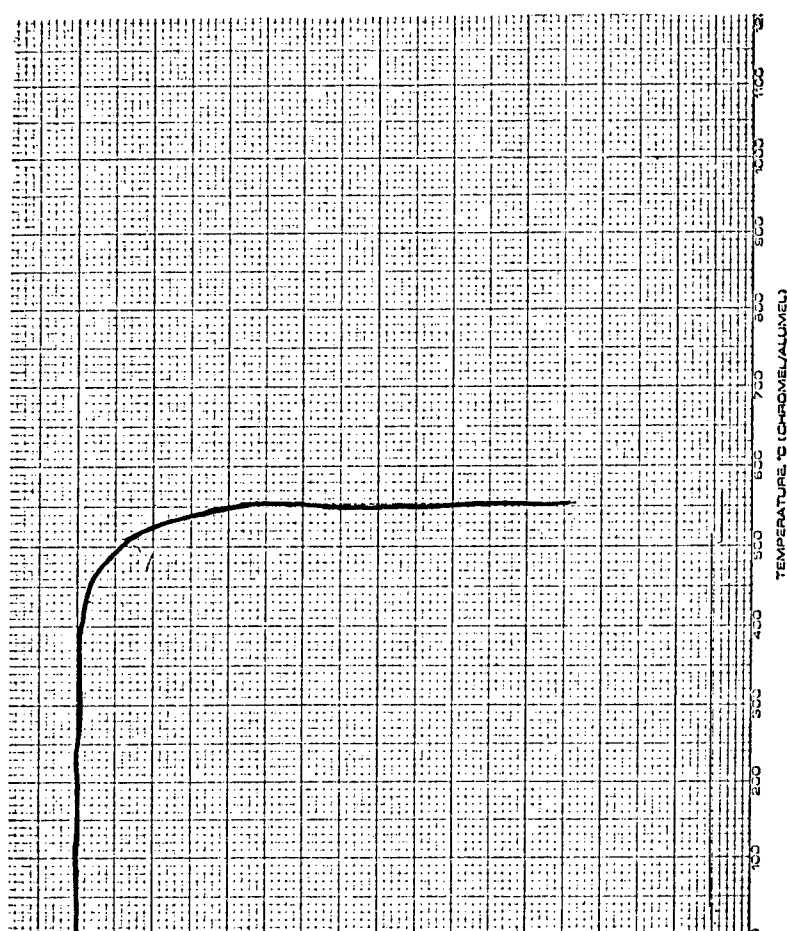Figure 29. TGA Thermogram of Compound 105 (Nitrogen).

TEMPERATURE °C (CHROMEL/ALUMEL)

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